IN THE UNITED STATES DISTRICT COURT
FOR THE DISTRICT OF DELAWARE

LIQWD, INC., and OLAPLEX LLC, Plaintiffs, v. L'ORÉAL USA, INC., L'ORÉAL USA PRODUCTS, INC., L'ORÉAL USA S/D, INC., and REDKEN 5TH AVENUE NYC, L.L.C., Defendants.	CIVIL ACTION NO. 17-14 (JFB) (SRF) **DEMAND FOR JURY TRIAL** REDACTED -- PUBLIC VERSION Original Filing Date: January 31, 2019 Redacted Filing Date: June 20, 2019

THIRD AMENDED COMPLAINT

Plaintiffs Liqwd, Inc. ("Liqwd") and Olaplex LLC ("Olaplex") (collectively "Plaintiffs" or "Olaplex"), bring this action against L'Oréal USA, Inc.; L'Oréal USA Products, Inc.; L'Oréal USA S/D, Inc.; and Redken 5th Avenue NYC, L.L.C. (collectively, "L'Oréal") for infringing Plaintiffs' exclusive rights under the Patent Laws of the United States (35 U.S.C. § 1 *et seq.*), misappropriating Olaplex's trade secrets, and breaching a non-disclosure agreement. The infringing products are the Matrix Bond Ultim8, Redken pH-Bonder, and L'Oréal Professionnel Smartbond 3 step systems (collectively, "Accused Products"). Olaplex alleges upon personal knowledge as to its own activities and upon information and belief as to the activities of others and all other matters, and state as follows:

NATURE OF THE ACTION / INTRODUCTION

1. L'Oréal is the world's largest beauty company and reported over $27 billion in revenue during its last fiscal year.

2. A small California start-up called Olaplex recently discovered, developed, and eventually began selling a novel, game-changing product to the professional hair care market. One of Olaplex's three current products is the Olaplex Bond Multiplier No. 1 ("Bond Multiplier"), which protects hair during bleach treatments, and has quickly become a favorite treatment of hair care professionals. As of October 2016, hundreds of thousands of stylists in more than 80 countries have used Olaplex, and it is widely acclaimed to have revolutionized the hair care industry.

3. The effect of using Olaplex during bleach treatments is readily apparent from a side-by-side picture of bleached hair with and without Olaplex. In the picture below, the left swatch of hair is an unprocessed color treated hair sample, the middle swatch of hair is the same color treated hair sample after being subjected to foil bleaching, rinsing, conditioning, and drying, and the right swatch of hair is the same color treated hair sample after foil bleaching with Olaplex Bond Multiplier added, rinsing, treating with Olaplex Bond Perfector (No. 2), rinsing, shampooing, conditioning, and drying.

4. Bond Multiplier's remarkable performance and the extremely positive response of hair care professionals to the product spurred L'Oréal to approach Olaplex in 2015. Under the guise of a potential acquisition of Olaplex, L'Oréal received access to non-public, confidential, and proprietary information from Olaplex about its technology.

5. After receiving that confidential information L'Oréal ceased pursuing an acquisition of Olaplex. Instead, L'Oréal willfully took and copied Olaplex's technology without authorization to create three slavish "me too" knockoffs that are the subject of this action.

THE PARTIES

6. Plaintiff Liqwd is a California corporation, with its principal place of business in Santa Barbara, California.

7. Plaintiff Olaplex is a California limited liability company, with its principal place of business in Santa Barbara, California.

8. Defendant L'Oréal USA, Inc., ("L'Oréal USA, Inc.") is a Delaware corporation, headquartered at 10 Hudson Yards, New York, New York.

9. Defendant L'Oréal USA Products, Inc., ("L'Oréal USA Products, Inc.") is a Delaware corporation, headquartered at 10 Hudson Yards, New York, New York, and is a subsidiary of L'Oréal USA, Inc.

10. Defendant L'Oréal USA S/D, Inc., ("L'Oréal USA S/D, Inc.") is a Delaware corporation, headquartered at 10 Hudson Yards, New York, New York, and is a subsidiary of L'Oréal USA, Inc.

11. Defendant Redken 5th Avenue NYC L.L.C., ("Redken") is a New York limited liability company, headquartered at 10 Hudson Yards, New York, New York, and is a subsidiary of L'Oréal USA, Inc.

12. L'Oréal USA, Inc., L'Oréal USA Products, Inc., L'Oréal USA S/D, Inc., and Redken are engaged in the business of manufacturing and distributing

hair care products under the "Matrix," "Redken," and "L'Oréal Professionnel" brand names.

JURISDICTION AND VENUE

13. This is an action for patent infringement arising under the patent laws of the United States, 35 U.S.C. § 1 *et seq.*, including §§ 271 and 281. This Court has original jurisdiction under 28 U.S.C. §§ 1331 and 1338(a) over the patent-infringement claim and claim for misappropriation of trade secrets under the Defend Trade Secrets Act of 2016, 18 U.S.C. § 1836, as amended.

14. This Court has supplemental jurisdiction over Olaplex's state law claims pursuant to 28 U.S.C. § 1367. The federal and state claims alleged herein are so related that they form part of the same case or controversy. Examples (not comprehensive) of the relation of patent versus non-patent claims include the following: L'Oréal's misappropriation of Olaplex's trade secret information, including, but not limited to, information contained in confidential, unpublished patent application which led to the patents-in-suit; damages for Olaplex's patent infringement will similarly also require an inquiry into facts regarding development, marketing and sales of overlapping, competitive products. Thus, judicial economy, convenience, and fairness to the parties will result if this Court asserts jurisdiction over the state claims.

15. This Court has personal jurisdiction over L'Oréal. Three of the defendants are Delaware corporations. In addition, on information and belief, L'Oréal has transacted business in this District, contracted to supply goods or services in this District directly or through its agents, has offered for sale, sold and/or advertised its products and services in this District, and has otherwise purposely availed itself of the privileges and benefits of the laws of the State of Delaware. In addition, this Court has jurisdiction over L'Oréal USA, Inc., because L'Oréal USA, Inc. expressly consented to the exclusive jurisdiction of Delaware

courts over any dispute arising out of a non-disclosure agreement executed by the parties, effective May 15, 2015.

16. Venue is proper in this judicial district under at least 28 U.S.C. §§ 1391 and 1400(b). L'Oréal has one or more regular and established places of business in this judicial district, and/or has transacted business in this district. For example, L'Oréal USA Products and L'Oréal USA S/D are incorporated in the State of Delaware. L'Oréal is responsible for acts of infringement occurring in the District of Delaware, as alleged in this Complaint, and has delivered or caused to be delivered infringing products or services in the District of Delaware. L'Oréal also has caused the infringing products to be advertised, promoted, and sold in this judicial district. In addition, venue is proper in this District because L'Oréal USA, Inc., irrevocably consented to venue of any suit in Delaware courts, including any defense of inconvenient forum in a non-disclosure agreement executed by the parties, effective May 15, 2015.

BACKGROUND

Olaplex & Its Proprietary Hair Care Technology

17. Olaplex is a small company based in Santa Barbara, California that develops professional hair care products. Olaplex created the first successful and effective product in the hair "bond building" market, and it is the world leader in that market.

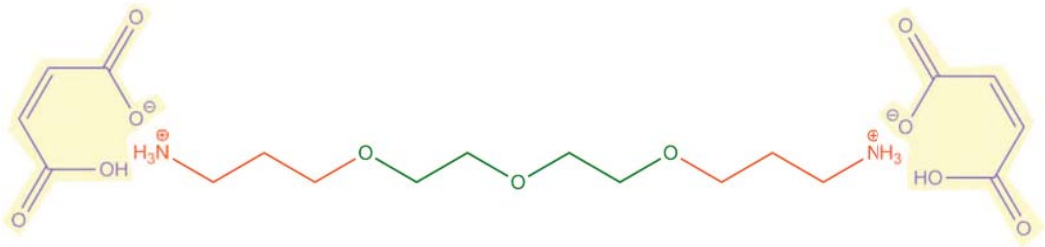
18. Bleaching is a common chemical treatment performed to lighten or remove color from hair, but it can be extremely harsh on hair. It can give hair a straw-like texture with fragile hair fibers that break easily. If bleach is allowed to stay on the hair too long, it can cause hair to melt (disintegrate), or even to fall out.

19. Repairing damaged hair has long been a shared concern of hair care professionals and their clients. Prior to Olaplex, hair care professionals lived with the fear that bleaching could ruin their client's hair.

20. Dean Christal grew up in the beauty business with his mother running a hair salon out of his childhood home, and his father was a distributor of beauty products in the Midwest. Mr. Christal also gained experience in the haircare and beauty industries by working with his brother, Don Christal, who had founded Alterna Haircare and California Tan (sunless tanner). With this background and an entrepreneurial spirit, Mr. Christal met Dr. Craig Hawker and Dr. Eric Pressley and urged them to tackle the holy grail of hair product development—figuring out how to keep chemical treatments from damaging hair.

21. Working literally in Dr. Pressly's home garage, Drs. Hawker and Pressly came up with the revolutionary technology to protect hair during chemical treatments.

22. This first-of-a-kind approach used a special "binding agent" or active ingredient to protect the hair during chemical treatments (like bleaching). The active ingredient of the Bond Multiplier product is a chemical called "bis-aminopropyl diglycol dimaleate" and whose chemical structure is shown below:



Olaplex's Patents

23. Olaplex initially filed applications (and ultimately obtained patents) describing the dimaleate active ingredient used in the Bond Multiplier product.

24. Recognizing the opportunity for unscrupulous competitors to copy Olaplex's proprietary technology and to use less expensive ingredients, Olaplex also obtained additional patents.

25. Two of these additional patents are United States Patent Nos. 9,498,419 and 9,668,954 (collectively, the "Asserted Patents"), entitled "Keratin Treatment Formulations and Methods." The '419 Patent was duly and legally issued by the United States Patent and Trademark Office on November 22, 2016. A copy of the '419 Patent is attached hereto as Exhibit A. The '954 Patent was duly and legally issued by the United States Patent and Trademark Office on June 6, 2017. A copy of the '954 Patent is attached hereto as Exhibit B.

26. Plaintiff Liqwd is the owner of the Asserted Patents. Plaintiff Olaplex is the exclusive licensee of the Asserted Patents with full rights of enforcement and recovery, including the right to pursue recovery of royalties and damages for infringement of the Asserted Patents.

27. Each claim of the Asserted Patents is valid and enforceable.

28. The Asserted Patents' claims describe, *inter alia*, methods for bleaching hair using maleic acid.

Olaplex Pioneers Bond Building in 2014

29. In early 2014, Olaplex was only available to select premier hair colorists. Among such premier hair colorists, Tracey Cunningham (a Redken Global Creative Consultant), Guy Tang (a social media superstar with more than a million followers online), and Riawna Capri (a celebrity stylist and co-owner of the Nine Zero One Salon in West Hollywood) began using Olaplex with their clients and friends (including celebrities like Jennifer Lopez and Gwyneth Paltrow), and also spreading the word about the "miracle product" Olaplex.

30. In May 2014, Beauty Launchpad (a national trade magazine) published a one-page feature on Olaplex, entitled "The Power of One." The article

describes how Olaplex can be used to help hair when it is being lightened (bleached). Ms. Cunningham is quoted in the article saying that "[y]ou still use your same hair color, your same products, your same technique, and your same shampoos and conditioners, but the hair is stronger and shinier."

31. The first step ("No. 1") is the Bond Multiplier product that is used, for example, in lightening (bleaching) treatments. The second step ("No. 2") is the "Bond Perfector" and is a cream that is applied after chemical processing of the hair and before it is shampooed and/or conditioned. The third step ("No. 3") is the "Hair Perfector," and is designed for at-home use in between visits to the hair salon.

32. Olaplex formally launched in June 2014 via the Olaplex.com website. In the first month, customers placed more than 1,500 orders for Olaplex products. The next month, that number of orders nearly doubled. More than 20,000 orders for Olaplex products were fulfilled on Olaplex.com alone in the first six months. This success came at a time when Olaplex did not have any full-time employees and had not done any traditional advertising.

33. In November 2014, Olaplex launched in the United States with one of the largest wholesale salon and beauty supply distributors in the country, Salon Centric (a wholly-owned subsidiary of Defendant L'Oréal USA, Inc.). Salon Centric opened some 100,000 accounts with Olaplex in the first six months. Olaplex generated literally millions of dollars of sales for Salon Centric in that short period.

34. Olaplex also has been the subject of numerous stories in leading national and international publications, such as Allure, Beauty Now, British Vogue, Cosmopolitan, Daily Mail, Elle, Fashion Quarterly, Glamour Russia, Harper's Bazaar, Huffington Post, Marie Claire, Modern Salon, MTV News, New York Magazine, New York Times, People Magazine, Pop Sugar, Refinery 29, U.S.

Weekly, Vanity Fair Italia, Vogue Germany, Vogue India, Washingtonian, and Women's Health. This partial list highlights the remarkable results that can be achieved with Olaplex's innovative professional hair care technology and the dramatic influence that Olaplex is having on the hair care industry.

35. Today, Bond Multiplier has been used by hundreds of thousands of stylists across the globe, and continues to receive industry awards and rave reviews. In March 2015, Olaplex won the category "Favorite Color Innovation (Tool or Treatment)" at the 15th Annual Stylist Choice Awards. At this year's Stylist Choice Awards, Olaplex won two categories: "Favorite Bond Rebuilder" and "Favorite Product You Can't Live Without."

36. Olaplex has an incredible presence and following on social media, with many of the top personalities in the entertainment industry showcasing their love of Olaplex. Below are un-solicited posts about Olaplex from celebrities Kim Kardashian West and supermodel Molly Sims:

L'Oréal Receives Olaplex's Confidential Information and then Ends Acquisition Talks

37. L'Oréal is in the business of selling, among other things, professional hair care products. Despite its long history, L'Oréal has never managed to successfully create the holy grail of hair product development—figuring out how to keep chemical treatments (like lightening or bleaching) from damaging hair.

38. As word spread about the Olaplex "miracle treatment" and as Olaplex's sales skyrocketed (including through L'Oréal's Salon Centric distribution arm), L'Oréal became interested in learning more about Olaplex and how it worked.

39. L'Oréal attempted to hire away Olaplex's key employees, whom L'Oréal believed were responsible for Olaplex's development. Drs. Hawker and Pressly were both contacted by a L'Oréal "Talent Acquisition" manager in March 2015 seeking to discuss their backgrounds and potential opportunities at L'Oréal. Drs. Hawker and Pressly did not respond to L'Oréal's overtures.

40. In January 2015, Olaplex CEO Dean Christal was contacted by Paul Sharnsky, a senior vice president of L'Oréal subsidiary Salon Centric, regarding a potential acquisition of Olaplex.

41. On February 20, 2015, Mr. Christal attended a lunch meeting in New York City, that also included Bertrand Fontaine (President at Salon Centric – A

Division of L'Oréal USA) and Frédéric Rozé (L'Oréal's Executive Vice President for the America's Zone) to discuss the acquisition.

42. On information and belief, L'Oréal CEO Jean Paul Agon attended a meeting in New York City in early March 2015, at which he authorized the potential acquisition of Olaplex.

43. On or about March 27, 2015, Mr. Christal met in Paris with Hugo Kunetz (President Americas for L'Oréal PPD), An Verhulst-Santos (Director Professional Products at L'Oréal), and Nicolas Hieronimus (President, Selective Divisions L'Oréal), a trusted confidant of Mr. Agon.

44. On April 14, 2015, Mr. Christal and Roger Dolden (SVP Business Development, L'Oréal, USA, Inc.) held a meeting in Santa Monica, which was also attended by Mr. Sharnsky. In addition to asking for access to Olaplex's intellectual property, financials, and marketing strategy, Mr. Dolden pressed for an in-person meeting with Olaplex's chemists (Drs. Hawker and Pressly).

45. On May 13, 2015, Mr. Christal received an email from Mr. Dolden, attaching a non-disclosure agreement ("NDA"), effective May 15, 2015, and a preliminary list of due diligence requests, and a set of "illustrative talking points." L'Oréal codenamed the potential Olaplex acquisition as Project Olivia, and on occasion using Olivia interchangeably with Olaplex. The talking points, which were prepared by Delphine Allard (L'Oréal's International Director of Research and Innovation), requested detailed technical information in order to "[b]etter understand the chemistry behind [Olivia]." L'Oréal specifically asked Olaplex to disclose Olivia's "mechanism of action [and] interaction with hair fiber." L'Oréal also requested information about the "testing [Olaplex] did to develop/finalize the product," and the "tests [Olaplex] did to assess stability of their formula, specifically analytical stability of the active ingredient."

46. On or about May 15, 2015, the parties executed the NDA. Paragraph 12 of the NDA provides that the parties "irrevocably consent to the exclusive jurisdiction of any state or federal court located within the State of Delaware over any dispute arising out of or relating to this Agreement and the transactions contemplated hereby."

47. On or about May 19, 2015, and pursuant to the NDA, Olaplex provided to L'Oréal a copy of a then-unpublished patent application (Serial No. 14/713,885) describing the use of maleic acid during hair bleaching. The application, which ultimately led to issuance of the patent-in-suit, disclosed to L'Oréal the active ingredient and formula that would ultimately become the Accused Product, roughly six months before the application was published in German in Germany on October 8, 2015, and published in English in USA on November 16, 2015.

48. Just days prior to the May 19 meeting, Mr. Roger Dolden, EVP Mergers and Acquisitions for L'Oréal USA, requested that Mr. Christal provide information on Olaplex's technology, its efficacy, testing, intellectual property portfolio, and profit margin, amongst other things. During the May 19 meeting, Mr. Christal and Mr. Pressly endeavored to share all the information on Olaplex with Mr. Dolden, Kunetz, and Allard.

49. In an Interrogatory Response dated March 8, 2017, L'Oréal took the position that it did not have knowledge of the patent application (Serial No. 14/713,885) before November 19, 2015. Upon information and belief, Defendants are taking this position because the patent application was handed to Ms. Allard (an employee of L'Oréal S.A.) at the May 19 meetings. However, Olaplex notes that Mr. Dolden and Mr. Kunetz were present during the discussion relating to this application with Ms. Allard.

50. On May 19, 2015, Mr. Christal and Dr. Pressly met in person with several L'Oréal representatives, including Mr. Dolden, Mr. Kunetz, and Ms. Allard. During the meeting, which lasted approximately 4 hours, Dr. Pressly provided L'Oréal with information requested in L'Oréal's "illustrative" talking points, including an in-depth explanation of how the formula works and what testing is needed to ensure efficacy. The parties also discussed various financial items listed in L'Oréal's preliminary due diligence requests.

51. L'Oréal representatives initially met with Mr. Christal individually for approximately 1-2 hours, and then met with Mr. Christal and Dr. Pressly jointly for the remainder of the meeting to discuss the technology. During the joint meeting with Mr. Christal and Dr. Pressly, L'Oréal's representatives had before them a binder with documents as well as copies of Olaplex's patents/patent applications, and sought to question Dr. Pressly about the technology. L'Oréal asked about Olaplex's patents, the chemistry behind the products, whether the active ingredient was stable in the bottled product, and how Olaplex arrived at the ideal concentration of the active ingredient. Testing was also a major focus of the discussion, with Dr. Pressly explaining the method and results of Olaplex's tensile tests, scanning electron microscope tests, and nuclear magnetic resonance tests.

52. The May 19 meeting provided L'Oréal with a significant amount of trade secret and confidential information, all of which was provided to L'Oréal by Olaplex pursuant to the terms of the NDA.

53. This trade secret and confidential information included [redacted]

[redacted]

54. [redacted]

55. [redacted]

[redacted] All of this testing information was immensely valuable, given that a major impediment to commercializing any hair product is the time and effort involved in effectively testing the product.

56. Between the confidential, unpublished patent application that disclosed maleic acid as the active ingredient, and the additional technical details provided by Dr. Pressly at the May 19 meeting, L'Oréal gained all the information needed to bring a competitive infringing product to market in a short span of time.

57. Dr. Pressly's detailed explanation of Olaplex's testing results allowed L'Oréal to drastically reduce the amount of testing required, a process that can easily take years (given that this was an entirely new category for L'Oréal to enter) and costs substantial amount of money. At the time of the disclosure to L'Oréal, all of this information — the formula, the testing methodology and results — was protected as trade secrets and subject to reasonable efforts to main secrecy. Olaplex would not have disclosed this information to L'Oréal absent the NDA, which L'Oréal violated by using Olaplex's confidential information to develop knock-off products.

58. The effort by L'Oréal to acquire Olaplex continued for several more months. In June 2015, Mr. Christal shared with Mr. Dolden of L'Oréal Olaplex's profit and loss statement.

59. On September 1, 2015, Mr. Dolden travelled to Los Angeles to meet with Mr. Christal for the stated purpose of discussing L'Oréal's acquisition of Olaplex. At this meeting, Mr. Dolden informed Mr. Christal that L'Oréal was no longer interested in acquiring Olaplex.

L'Oréal Willfully Copies and Knocks-off Olaplex and its 3-Part System

60. After ceasing negotiations to acquire Olaplex, L'Oréal embarked on a scheme to create not one, but three, "me too" knock-offs that it hoped would

mimic Olaplex's success. These "me too" products include the Matrix Bond Ultim8 product ("Bond Ultim8"), the Redken pH-Bonder product ("pH-Bonder"), and the L'Oréal Professionnel Smartbond product ("Smartbond").

61. L'Oréal's Bond Ultim8, pH-Bonder, and Smartbond products are collectively referred to herein as the "L'Oréal Bond Builders." Each line of the L'Oréal Bond Builders has three products, which are described below. For purposes of clarity, as defined above, the term "Accused Products" in this Complaint refers to the L'Oréal Bond Builder 3 step systems.

62. The L'Oréal entities involved in this unlawful patent infringement are uniquely positioned to harm Olaplex. Since late 2014, a L'Oréal USA, Inc. subsidiary (Salon Centric) has distributed Olaplex in the United States. It had access to highly valuable insights and information about Olaplex (such as the identities of salon-level customers, order frequency, order amounts, customer feedback, and Olaplex's marketing and branding strategy). That valuable commercial information provided a real-time insider's view of the success of Olaplex in the marketplace. As a vertically integrated beauty company, L'Oréal has product development and manufacturing entities too. These entities could use commercial information obtained by Salon Centric to copy Olaplex and to attempt to usurp its unique position in the marketplace in a way that other companies could not.

63. For example, Salon Centric employees have been involved in efforts to promote the L'Oréal Bond Builders across the United States since their recent launch. In doing so, several employees have made false statements to consumers that the Olaplex technology patent had "run up" or was expired, "it was only available for two years," and the "secret recipe" was available for any company to utilize. These statements were made in several states. All three of Olaplex's

products (Bond Multiplier, Bond Perfector, and Hair Perfector) are patent protected.

64. L'Oréal copied the revolutionary three-step Olaplex system to protect hair during professional bleaching treatments. The marketing imagery produced by L'Oréal strongly resembles Olaplex's marketing materials, showing the product packaging in the background with the products lined up in front and somewhat off-center:

<table>
<tr><th colspan="3">ORIGINAL OLAPLEX</th></tr>
<tr><td colspan="3"> 
</td></tr>
<tr><th colspan="3">L'ORÉAL "ME TOO" KNOCKOFFS</th></tr>
<tr><td>Matrix
Bond Ultim8</td><td>Redken
pH-Bonder</td><td>L'Oréal
Professionnel
Smartbond</td></tr>
<tr><td> 
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65. Just like Olaplex (which has "No. 1", "No. 2" and "No. 3" products), the L'Oréal Bond Builders include three components. Bond Ultim8 products are labeled 1, 2, and 3. pH-Bonder products are labeled 1, 2, and "Post-Service Perfector." Smartbond products are labeled 1, 2 and "Conditioner" step 3.

66. Just like Olaplex, each of the three L'Oréal Bond Builders is sold as a kit containing the "1" and "2" products for use in a professional hair salon. Just like Olaplex, each kit includes a dosing dispenser (a syringe in the Bond Ultim8 and pH-Bonder kits, and a cup in the Smartbond kit). Just like Olaplex, L'Oréal sells the "step 3" or "Post-Service Perfector" products for home use by consumers (in between salon visits).

67. Olaplex is sold in two different size kits. Olaplex calls the larger one the "Salon Intro Kit." It calls the smaller one the "Travelling Stylist kit." Just like Olaplex, Bond Ultim8 and pH-Bonder are sold in two different size kits. Bond Ultim8 even uses similar names for its kits. The larger one is called the "Salon Intro Kit" (exactly the same name that Olaplex uses) and a smaller one is called the "Travel Kit" (a very similar name to the one that Olaplex uses).

68. The Accused Products are direct competitors of Olaplex' Bond Multiplier.

69. With Olaplex, hair care professionals use Bond Multiplier at the salon to protect hair during bleach treatments. The Accused Products are aimed at the very same end consumers. The Bond Ultim8 Step 1 (Amplifier) is sold to hair care professionals as a way to prevent breakage and protect hair bonds during lightening services (bleaching). The pH-Bonder #1 (Bond Protecting Additive) and Smartbond Step 1 (Additive) also are for use by hair care professionals during lightening or bleaching hair treatments.

70. The Accused Products are marketed to these consumers as serving the same need as Bond Multiplier. Since its launch, Olaplex has taught professional hair stylists that Olaplex' Bond Multiplier will allow them to lighten their client's hair without compromising the integrity of the hair. L'Oréal employs very similar messaging with its Accused Products, touting that they protect bonds during

lightening, promote bond integrity during lightening, and strengthen bonds/hair during lightening.

71. Olaplex Bond Multiplier has four ingredients: water, the active ingredient (bis-aminopropyl diglycol dimaleate) and two preservatives (sodium benzoate and phenoxyethanol).

72. L'Oréal's Accused Products have very similar ingredients. Each of the Accused Products has the following ingredients: water, the active ingredient (maleic acid), a buffering agent (ethanolamine), and three dyes (CI 19140/Yellow 5, CI 14700/Red 4, CI 42090/Blue 1). The Accused Bond Ultim8 Step 1 Amplifier, and pH-Bonder #1 Bond Protecting Additive have one additional ingredient: citric acid. The Accused Products are applied to hair with a bleaching formulation. Although one or more of the ingredients may be a *product* colorant, the ingredients do not contain a hair coloring agent. In other words, the dyes exist to color the product itself, not to color hair. In fact, L'Oréal has conducted dye impact studies on its Accused Products and concluded that the "[d]yes added to the Bonding additive, at the very low concentration introduced, have the only properties to color the bulk of the additive but none properties to color hair":

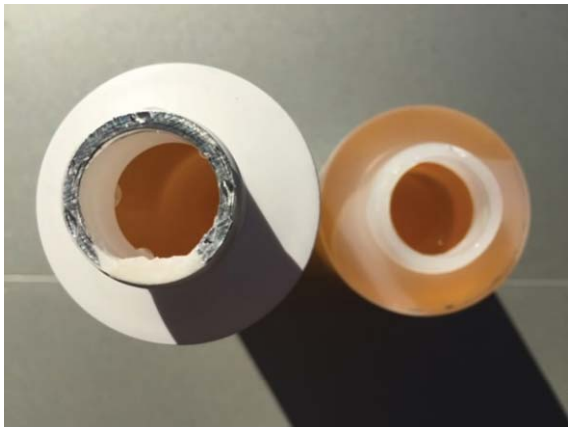
Impact of the dyes used in Bonding additive P4

Before treatment	**P4 1112405** Pilote FC 17/05/16	**P4 without dyes 1112405 B** BB200416	**P4 with a higher concentration of dyes 1112405 C** CS200716
Majirel clear			
IPLO			

CONCLUSION :

Dyes added into the Bonding additive, at the very low concentration introduced, have the only properties to color the bulk of the additive but none properties to color hair.

73. Olaplex became known shortly after it was launched as "liquid gold" due to its unique golden yellow color, which is visible through its translucent bottle. L'Oréal's Accused Products add three different dyes to achieve a color reminiscent of the original Olaplex Bond Multiplier No. 1 product. The pictures below show the Accused Bond Ultim8 Step 1 product (left) and Olaplex Bond Multiplier No. 1 (right) side-by-side and demonstrate the color similarity of the products in the bottles as used by hair care professionals:



74. The instructions for using Olaplex and L'Oréal Bond Builders are also very similar. For the Accused Products, the ratios of the product to the bleach or lightener used are virtually identical, and call for about 4 ml of the respective product for each 15 grams of lightening (bleach) powder:

ORIGINAL OLAPLEX INSTRUCTIONS[1]		
"For lightener in foils, add ¼ oz. (7.5ml) Olaplex No. 1 for 30-60g of lightener powder. For anything less, add ⅛ oz (3.75ml) Olaplex No. 1."		
INSTRUCTIONS FOR L'ORÉAL "ME TOO" KNOCKOFFS		
Matrix Bond Ultim8	Redken pH-Bonder	L'Oréal Professionnel Smartbond
"LIGHTENER: add 4ml (⅛ oz) of STEP 1 for every 15–30 grams (½–1 oz) of powder or 8ml (¼ oz.) of BOND ULTIM8 STEP 1 for every 30–60 grams (1–2 oz) of powder used in the mixture …."	"For lightener, add 4 ml of pH-Bonder #1 for every 15–30 grams (½ – 1 oz) of powder or 8 ml of pH-Bonder #1 for every 30–60 grams (1 – 2 oz) of powder used in mixture …."	"For lightener product, add 4ml (.14 oz) of Step 1 additive for every 15-30 g (½-1 oz) or 8ml of Step 1 additive for every 30-60 g (1-2 oz) of lightening product used in the final mixture …."

75. The original Olaplex is a two-step professional salon service with a white "Bond Perfector No. 2" cream being applied after chemical processing of the hair and before shampooing. L'Oréal copied that too in its Bond Builders. Matrix Bond Ultim8 "2" sealer, Redken pH-Bonder "fiber restorative pre-wash concentrate" "#2", and L'Oréal Professionnel Smart Bond pre-shampoo Step "2" are white creams applied after chemical processing of the hair and before it is shampooed and/or conditioned. L'Oréal's "2" products do not contain dyes.

[1] The written instructions for Olaplex changed in September 2016, and now instruct hair care professionals to use about half as much Bond Multiplier product during bleaching. L'Oréal copied the original Olaplex instructions dating back to just after the launch of the product (which are quoted throughout this Complaint), and L'Oréal has not yet updated its instructions to precisely match Olaplex's current instructions. (Although Olaplex changed its instructions, it was instructing users since late 2014 to use less Bond Multiplier product during bleach if they were not seeing appropriate lift (color lightening).

76. Again, L'Oréal's instructions tell hair care professionals to use its "me too" knockoff pre-wash cream / pre shampoo products in amounts and for times strikingly similar to the original Olaplex:

ORIGINAL OLAPLEX INSTRUCTIONS		
"Apply ½ oz (15 ml) of Bond Perfector from roots to ends. Comb thoroughly once. Leave on for a minimum of 5 minutes. For damaged hair, leave on for at least 10 minutes."		
INSTRUCTIONS FOR L'ORÉAL "ME TOO" KNOCKOFFS		
Matrix Bond Ultim8	Redken pH-Bonder	L'Oréal Professionnel Smartbond
"Apply 15ml–30ml (½–1oz) of STEP 2 SEALER depending on length and density of hair. Leave on the hair for a minimum of 10 minutes …."	"Depending on hair length and density, apply 15-30 g of pH-Bonder #2 into hair from roots to ends. Gently comb through once. Leave on for 10 minutes at room temperature …."	"2. Depending on hair length and density, apply 4 to 8 pumps of Step 2 pre shampoo into hair from roots to ends. 3. Comb through once to evenly distribute. 4. Leave on for 10 min at room temperature …."

77. The third component in the Olaplex system is the "Post-Service Perfector," which is for at-home use by customers in between visits to the hair salon. Again, the at-home components of the L'Oréal Bond Builders omit dyes entirely. Each is white and copies the appearance of Olaplex's "Hair Perfector." L'Oréal brazenly named the third (take home) component of its pH-Bonder product "Post-Service *Perfector*," again trying to benefit from the reputation of Olaplex's No. 3 "Hair *Perfector*" product.

78. Olaplex instructs that its Hair Perfector product should be used once a week and applied to unwashed towel-dried hair and left for at least 10 minutes. L'Oréal copied these instructions too:

ORIGINAL OLAPLEX INSTRUCTIONS	
"Apply a generous amount from roots to ends on unwashed towel-dried hair. Comb through once. Leave on for a minimum of 10 minutes or more."	
INSTRUCTIONS FOR L'ORÉAL "ME TOO" KNOCKOFFS	
Matrix Bond Ultim8	Redken pH-Bonder
"To be used once a week. Before shampoo, apply on wet, towel-dried hair. Massage into hair from roots to ends. Leave on for at least 10 minutes …."	"Before shampoo, apply on wet, towel-dried hair. Massage into hair from roots to ends. Leave on for at least 10 minutes …."

L'Oréal Was Aware of Olaplex's Patents and On Notice of Infringement

79. L'Oréal had actual knowledge of the Asserted Patents and/or the applications from which they claim priority prior to the California action, or willfully blinded itself to the existence of the Asserted Patents, and had actual knowledge of the Asserted Patents prior to the filing of this action.

80. L'Oréal monitors Olaplex's patents by, for example, monitoring websites having information regarding Olaplex's patents.

81. In or about May 2015, and under a non-disclosure agreement, L'Oréal USA, Inc. obtained in confidence from Olaplex a copy of a then-unpublished patent application (Serial No. 14/713,885). The Asserted Patents are related to this application and share the same disclosure.

82. L'Oréal also demonstrated its awareness of Olaplex's patents (and/or its pending applications) by statements it made to the public. L'Oréal has affirmatively and repeatedly told the public that maleic acid "alone" cannot be patented in an attempt to mislead that public that its "me too" knockoffs were lawful. However, L'Oréal knew that Olaplex had been patented and that Olaplex was continuing to patent the use of that ingredient in a specific bleaching method that L'Oréal had copied.

83. The ‘419 Patent issued from a patent application that was assigned Serial No. 15/087,415 by the U.S. Patent & Trademark Office (USPTO). A series of anonymous submissions were made to the USPTO on August 25, 2016, August 29, 2016, September 14, 2016, and September 23, 2016, which alleged the pending claims could not be allowed.

84. On information and belief, L’Oréal made one or more of those third party submissions to USPTO in hopes of stopping issuance of the ‘419 patent.

85. Those third party submissions were not successful. After the independent patent examiner carefully considered each third party submission, the ‘419 patent issued.

86. In any event, L’Oréal has had actual knowledge of the Asserted ‘419 Patent no later than the November 22, 2016 filing date of the original Complaint in California, Case 2:14-cv-08708 (“the California Action”), which has now been dismissed. L’Oréal has had actual knowledge of the Asserted ‘954 Patent no later than June 12, 2017, when Olaplex informed L’Oréal that it was going to move to amend the First Amended Complaint in this action to add a claim for infringement of the ‘954 Patent. In addition, L’Oréal admitted during discovery that Defendants became aware of U.S. App. No. 15/087,416 that gave rise to the ‘419 Patent no later than July 21, 2016; U.S. Pat. No. 9,326,926 parent patent to the ‘419 Patent (which shares the same specification) no later than May 3, 2016; and U.S. App. No. 14/713,885 that gave rise to the ‘926 Patent no later than November 19, 2015.

87. L’Oréal also admits being on notice that it would be and now is infringing the Asserted Patents. L’Oréal admitted during discovery that it received a letter from Olaplex on or about July/August 2016 informing it that the Accused Products infringe Olaplex’s intellectual property rights covering methods for bleaching hair with products containing maleic acid and maleic salts. L’Oréal

admits that it knew from this letter that if and when L'Oréal launched the Accused Products it would be sued by Olaplex for patent infringement.

88. L'Oréal also admits since the Asserted Patents have issued it has continued to make, use, offer for sale, and sell the Accused Products, and has continued to demonstrate use of the Accused Products and market and educate others how to use the Accused Products in accordance with their infringing instructions for bleaching treatments, deploying more than 600 artists in the U.S. to train others on infringing use of the Accused Products on a regular basis. L'Oréal also admits since the Asserted Patents have issued that it is L'Oréal's intention and desire when making, using, offering for sale, selling, demonstrating use, marketing and educating others how to use the Accused Products that third party users of the Accused Products follow L'Oréal's infringing instructions for bleaching treatments.

89. L'Oréal continues its willful infringing conduct despite having this knowledge.

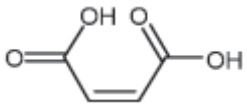
FIRST CAUSE OF ACTION

(Patent Infringement of the '419 Patent, 35 U.S.C. §§ 1 *et seq.*)

90. Olaplex realleges and incorporates herein by reference the allegations contained in the preceding paragraphs.

91. Claim 1 of the Asserted '419 Patent reads as follows:

1. A method for bleaching hair comprising:

> (a) mixing a formulation comprising an active agent with a bleaching formulation, wherein the active agent has the formula:
>
> 
>
> or salts thereof; and
>
> (b) applying the mixture to the hair;

> wherein the active agent in the mixture is at a concentration ranging from about 0.1% by weight to about 50% by weight; and
>
> wherein the mixture does not contain a hair coloring agent.

92. L'Oréal's Accused Products are used during hair bleaching. Defendant Redken's website (www.redken.com) describes one of the Accused Products as follows: "pH-Bonder is a unique synergistic system that helps protect bonds and reduce breakage during technical services (such as bleach and hair color)." The instructions that accompany the pH-Bonder product describe how to use it during bleaching treatment.

93. L'Oréal has produced training videos showing its employees using the Accused Products during bleaching and encouraging others to do the same, which L'Oréal maintains and continues to broadcast after the Asserted '419 Patent issued, including the following marketing videos uploaded by "Redken 5th Avenue NYC":

> https://www.YouTube.com/watch?v=0hwc44b2B4E (uploaded October 3, 2016) ("pH-Bonder YouTube Video"); and
>
> https://www.periscope.tv/Redken5thAve/1YqxoXpbPVbKv? ("pH-Bonder Periscope Video")

94. Sean Goddard, a Global Redken Artist and Artistic Trainer, appears in both the pH-Bonder YouTube video and the pH-Bonder Periscope Video. Upon information and belief, Mr. Goddard and other L'Oréal stylists, colorists and trainers continue to infringe the Asserted '419 Patent by producing videos and showing employees how to use the Accused Products during bleaching and encouraging others to do the same after the Asserted '419 Patent issued.

95. In training hair care professionals how to use the pH-Bonder product, L'Oréal teaches the "pH-Bonder regime" which the pH-Bonder YouTube video

describes as "a complete synergistic system" to "promote bond integrity" during lightening (the word that L'Oréal uses instead of bleaching).

96. YouTube marketing videos uploaded by "L'Oréal Professionnel," which L'Oréal maintains and continues to broadcast after the Asserted '419 Patent issued, show and describe how to use Smartbond during bleaching treatments to maintain the integrity of the hair:

https://www.youtube.com/watch?v=SHaJTzM5xu8 (uploaded August 2, 2016);

https://www.youtube.com/watch?v=i1Ch8lzdjeI (uploaded August 2, 2016);

https://www.youtube.com/watch?v=4ToTc4Q5x3I (uploaded August 24, 2016); and

https://www.youtube.com/watch?v=5BU8Nm74ERI (uploaded November 18, 2016) (collectively "Smartbond YouTube Videos")

97. YouTube marketing videos uploaded by "Matrix," which L'Oréal maintains and continues to broadcast after the Asserted '419 Patent issued, show and describe how to use Bond Ultim8 during bleaching treatments to maintain the integrity of the hair:

https://www.youtube.com/watch?v=DqxLGHbzQXQ (uploaded November 17, 2016); and

https://www.youtube.com/watch?v=z_PO-85XxZE (uploaded November 29, 2016) ("Matrix YouTube Videos")

98. L'Oréal instructs hair care professionals to use the Accused Products with lightener powder (bleach) as set forth above in paragraph 72.

99. L'Oréal, or those under L'Oréal's direction and control, have maintained and continued to broadcast the aforementioned Internet videos up online for the duration of the Asserted '419 Patent's post-issuance term.

100. L'Oréal's instructions and training describe the amounts of the Accused Products, powder bleach, and developer to use. The instructions which accompany the Bond Ultim8 Step 1 (Amplifier) and the pH-Bonder #1 (Bond Protecting Additive) advise to use 15-90 ml of developer with 15-30 g of bleach powder and 4 ml of the Bond Ultim8 Step 1 (Amplifier) and the pH-Bonder #1 (Bond Protecting Additive), and to use 30-120 ml of developer with 30-60 g of bleach powder and 8 ml of the Bond Ultim8 Step 1 (Amplifier) and the pH-Bonder #1 (Bond Protecting Additive). The instructions which accompany the Smartbond Step 1 (Additive) advise to use 15–30 g of bleach powder and 4 ml of the Smartbond Step 1 (Additive), and to use 30–60 g of bleach powder and 8 ml of the Smartbond Step 1 (Additive). The instructions which accompany the Smartbond Step 1 (Additive) advise to use mixing ratios of 1:1, 1:1.5, or 1:2. The mixing ratio is the ratio of powder bleach to developer.

101. The pH-Bonder YouTube video describes that the "#1 bond protecting additive" has "maleic acid" that "acts as a magnet to attract and then remove ions from the lighteners that interfere with weak [hair] bonds." In this video, Mr. Goddard:

- instructs hair care professionals to add and mix the #1 Bond Protecting Additive directly into their lightening formula, and actually shows this being done; and
- admits "of course" we put pH-Bonder in our lightener when lightening and color treating a model's hair, as shown on the video.

102. The pH-Bonder YouTube video instructs users to mix 4 milliliters of "bond protecting additive solution" with 15–30 grams of powder lightener (i.e., bleach), or to mix 8 milliliters of "bond protecting additive solution" with 30–60 grams of bleach.

103. In one of the Smartbond YouTube videos, Johnny Ramirez (a L'Oréal Professionnel Hair Artist from Los Angeles) specifically instructs users to mix 30 grams of powder lightener (bleach) with 8 milliliters of Step 1 additive.

104. The Matrix YouTube videos specifically instruct users to mix Light Master powder lightener (bleach) with Bond Ultim8 Step 1 additive. For example, in one of the Matrix YouTube videos, Constance Robbins (a Matrix Artistic Educator) uses Bond Ultim8 Step 1 additive to pre-lighten hair with bleach before a coloring service.

105. The labeling provided with the Accused Products shows that each has the following ingredients: water, maleic acid, ethanolamine, CI 19140/Yellow 5, CI 14700/Red 4, CI 42090/Blue 1. The Accused Products are applied to hair with a bleaching formulation. Although one or more of the ingredients may be a product colorant, the ingredients do not contain a hair coloring agent.

106. On information and belief, the Material Safety and Data Sheets for L'Oréal's Accused Products express the amount of maleic acid present in these products as sold, and report concentrations of less than or equal to 10.7 weight percent.

107. When used according to L'Oréal's instructions and training, the concentration of maleic acid in the Accused Products is within a range from about 0.1% by weight to about 50% by weight in the bleaching formulation that is applied to the hair, as in claim 1 of the Asserted '419 Patent.

108. When used according to L'Oréal's instructions and training, the mixture of the Accused Products and the bleaching formulation does not contain a hair coloring agent.

109. When used according to L'Oréal's instructions and training, mixing of bleaching formulation and the maleic acid additive occurs at a time of use and

prior to application of the mixture to the hair, as in claim 10 of the Asserted '419 Patent.

110. L'Oréal admits since the Asserted Patents have issued that it has continued to make, use, offer for sale, and sell the Accused Products, and has continued to demonstrate use of the Accused Products and market and educate others how to use the Accused Products in accordance with their infringing instructions for bleaching treatments, deploying more than 600 artists in the U.S. to train others on infringing use of the Accused Products on a regular basis. L'Oréal also admits since the Asserted Patents have issued that it is L'Oréal's intention and desire when making, using, offering for sale, selling, demonstrating use, marketing and educating others how to use the Accused Products that third party users of the Accused Products follow L'Oréal's infringing instructions for bleaching treatments. As such, L'Oréal has and continues to directly infringe and actively induce infringement of the Asserted '419 Patent.

111. L'Oréal has directly infringed the Asserted '419 Patent, including at least claims 1 and 10, and continues to do so. L'Oréal has infringed at least these claims of the Asserted '419 Patent, either literally and/or under the doctrine of equivalents, by using, selling, or offering to sell in the United States, and/or importing in the United States, the Accused Products without authority from the patent holder. L'Oréal is liable for direct infringement of the Asserted '419 Patent pursuant to 35 U.S.C. § 271(a).

112. L'Oréal also has actively induced others to infringe the Asserted '419 Patent, including at least claims 1 and 10, and continues to do so. L'Oréal had knowledge of the Asserted '419 Patent prior to, or at least as of, the filing of the California Action on November 22, 2016 and had knowledge that use of the Accused Products infringes, either literally and/or under the doctrine of equivalents, at least claims 1 and 10 of the Asserted '419 Patent. L'Oréal has

induced direct infringement of the Asserted '419 Patent by L'Oréal's customers, resellers, retailers, and end users by intentionally directing them and encouraging them to use, sell, and/or offer to sell within the United States and/or to import into the United States the Accused Products. L'Oréal provides written instructions, video tutorials, and otherwise instructs its customers how to use the Accused Products in an infringing manner. L'Oréal is liable for indirect infringement of the Asserted '419 Patent pursuant to 35 U.S.C. § 271(b).

113. Unless enjoined by this Court, L'Oréal will continue to infringe the Asserted '419 Patent and to actively induce others to infringe the Asserted '419 Patent, and Olaplex will continue to suffer irreparable harm for which there is no adequate remedy at law. Accordingly, Olaplex is entitled to preliminary and permanent injunctive relief against such infringement pursuant to 35 U.S.C. § 283.

114. As a direct and proximate result of L'Oréal's infringement, Olaplex has been and continues to be irreparably injured in its business and property rights, and is entitled to appropriate relief and to recover damages for such injuries pursuant to 35 U.S.C. § 284 in an amount to be proven at trial.

SECOND CAUSE OF ACTION

(Patent Infringement of the '954 Patent, 35 U.S.C. §§ 1 *et seq.*)

115. Olaplex realleges and incorporates herein by reference the allegations contained in the preceding paragraphs.

116. Claim 1 of the Asserted '954 Patent reads as follows:

1. A method for bleaching hair comprising:

> (a) mixing a bleach powder and a developer to form a bleaching formulation;
>
> (b) mixing an active agent formulation comprising an active agent with the bleaching formulation to form a mixture, wherein the active agent is maleic acid; and

(c) applying the mixture to the hair;

wherein the active agent in the mixture is at a concentration ranging from about 0.1% by weight to about 50% by weight.

117. L'Oréal's Accused Products are used during hair bleaching. Defendant Redken's website (www.redken.com) describes one of the Accused Products as follows: "pH-Bonder is a unique synergistic system that helps protect bonds and reduce breakage during technical services (such as bleach and hair color)." The instructions that accompany the pH-Bonder product describe how to use it during bleaching treatment.

118. L'Oréal has produced training videos showing its employees using the Accused Products during bleaching and encouraging others to do the same, which L'Oréal maintains and continues to broadcast after the Asserted Patents issued, including the following marketing videos uploaded by "Redken 5th Avenue NYC":

https://www.YouTube.com/watch?v=0hwc44b2B4E (uploaded October 3, 2016) ("pH-Bonder YouTube Video"); and

https://www.periscope.tv/Redken5thAve/1YqxoXpbPVbKv? ("pH-Bonder Periscope Video")

119. Sean Goddard, a Global Redken Artist and Artistic Trainer, appears in both the pH-Bonder YouTube video and the pH-Bonder Periscope Video. Upon information and belief, Mr. Goddard and other L'Oréal stylists, colorists and trainers continue to infringe the Asserted '954 Patent by producing videos and showing employees how to use the Accused Products during bleaching and encouraging others to do the same after the Asserted '954 Patent issued.

120. In training hair care professionals how to use the pH-Bonder product, L'Oréal teaches the "pH-Bonder regime" which the pH-Bonder YouTube video

describes as "a complete synergistic system" to "promote bond integrity" during lightening (the word that L'Oréal uses instead of bleaching).

121. YouTube marketing videos uploaded by "L'Oréal Professionnel," which L'Oréal maintains and continues to broadcast after the Asserted '954 Patent issued, show and describe how to use Smartbond during bleaching treatments to maintain the integrity of the hair:

https://www.youtube.com/watch?v=SHaJTzM5xu8 (uploaded August 2, 2016);

https://www.youtube.com/watch?v=i1Ch8lzdjeI (uploaded August 2, 2016);

https://www.youtube.com/watch?v=4ToTc4Q5x3I (uploaded August 24, 2016); and

https://www.youtube.com/watch?v=5BU8Nm74ERI (uploaded November 18, 2016) (collectively "Smartbond YouTube Videos")

122. YouTube marketing videos uploaded by "Matrix," which L'Oréal maintains and continues to broadcast after the Asserted '954 Patent issued, show and describe how to use Bond Ultim8 during bleaching treatments to maintain the integrity of the hair:

https://www.youtube.com/watch?v=DqxLGHbzQXQ (uploaded November 17, 2016); and

https://www.youtube.com/watch?v=z_PO-85XxZE (uploaded November 29, 2016) ("Matrix YouTube Videos")

123. L'Oréal instructs hair care professionals to use the Accused Products with lightener powder (bleach) as set forth above in paragraph 72.

124. L'Oréal, or those under L'Oréal's direction and control, have maintained and continued to broadcast the aforementioned Internet videos up online for the duration of the Asserted '954 Patent's post-issuance term.

125. L'Oréal's instructions and training describe the amounts of the Accused Products, powder bleach, and developer to use. The instructions which accompany the Bond Ultim8 Step 1 (Amplifier) and the pH-Bonder #1 (Bond Protecting Additive) advise to use 15-90 ml of developer with 15-30 g of bleach powder and 4 ml of the Bond Ultim8 Step 1 (Amplifier) and the pH-Bonder #1 (Bond Protecting Additive), and to use 30-120 ml of developer with 30-60 g of bleach powder and 8 ml of the Bond Ultim8 Step 1 (Amplifier) and the pH-Bonder #1 (Bond Protecting Additive). The instructions which accompany the Smartbond Step 1 (Additive) advise to use 15–30 g of bleach powder and 4 ml of the Smartbond Step 1 (Additive), and to use 30–60 g of bleach powder and 8 ml of the Smartbond Step 1 (Additive). The instructions which accompany the Smartbond Step 1 (Additive) advise to use mixing ratios of 1:1, 1:1.5, or 1:2. The mixing ratio is the ratio of powder bleach to developer.

126. The pH-Bonder YouTube video describes that the "#1 bond protecting additive" has "maleic acid" that "acts as a magnet to attract and then remove ions from the lighteners that interfere with weak [hair] bonds." In this video, Mr. Goddard:

- instructs hair care professionals to add and mix the #1 Bond Protecting Additive directly into their lightening formula, and actually shows this being done; and
- admits "of course" we put pH-Bonder in our lightener when lightening and color treating a model's hair, as shown on the video.

127. The pH-Bonder YouTube video instructs users to mix 4 milliliters of "bond protecting additive solution" with 15–30 grams of powder lightener (i.e., bleach), or to mix 8 milliliters of "bond protecting additive solution" with 30–60 grams of bleach.

128. In one of the Smartbond YouTube videos, Johnny Ramirez (a L'Oréal Professionnel Hair Artist from Los Angeles) specifically instructs users to mix 30 grams of powder lightener (bleach) with 8 milliliters of Step 1 additive.

129. The Matrix YouTube videos specifically instruct users to mix Light Master powder lightener (bleach) with Bond Ultim8 Step 1 additive. For example, in one of the Matrix YouTube videos, Constance Robbins (a Matrix Artistic Educator) uses Bond Ultim8 Step 1 additive to pre-lighten hair with bleach before a coloring service.

130. The labeling provided with the Accused Products shows that each has the following ingredients: water, maleic acid, ethanolamine, CI 19140/Yellow 5, CI 14700/Red 4, CI 42090/Blue 1. The Accused Products are applied to hair with a bleaching formulation.

131. On information and belief, the Material Safety and Data Sheets for L'Oréal's Accused Products express the amount of maleic acid present in these products as sold, and report concentrations of less than or equal to 10.7 weight percent.

132. When used according to L'Oréal's instructions and training, the concentration of maleic acid in the Accused Products is within a range from about 0.1% by weight to about 50% by weight in the bleaching formulation that is applied to the hair, as in claim 1 of the Asserted '954 Patent.

133. When used according to L'Oréal's instructions and training, the mixture of the Accused Products and the bleaching formulation does not contain a hair coloring agent.

134. L'Oréal admits since the Asserted Patents have issued that it has continued to make, use, offer for sale, and sell the Accused Products, and has continued to demonstrate use of the Accused Products and market and educate others how to use the Accused Products in accordance with their infringing

instructions for bleaching treatments, deploying more than 600 artists in the U.S. to train others on infringing use of the Accused Products on a regular basis. L'Oréal also admits since the Asserted Patents have issued that it is L'Oréal's intention and desire when making, using, offering for sale, selling, demonstrating use, marketing and educating others how to use the Accused Products that third party users of the Accused Products follow L'Oréal's infringing instructions for bleaching treatments. As such, L'Oréal has and continues to directly infringe and actively induce infringement of the Asserted '954 Patent.

135. L'Oréal has directly infringed the Asserted '954 Patent, including at least claim 1, and continues to do so. L'Oréal has infringed at least this claim of the Asserted '954 Patent, either literally and/or under the doctrine of equivalents, by using, selling, or offering to sell in the United States, and/or importing in the United States, the Accused Products without authority from the patent holder. L'Oréal is liable for direct infringement of the Asserted '954 Patent pursuant to 35 U.S.C. § 271(a).

136. L'Oréal also has actively induced others to infringe the Asserted '954 Patent, including at least claim 1, and continues to do so. L'Oréal had knowledge of the Asserted '954 Patent prior to, or at least as of, June 12, 2017 and had knowledge that use of the Accused Products infringes, either literally and/or under the doctrine of equivalents, at least claim 1 of the Asserted '954 Patent. L'Oréal has induced direct infringement of the Asserted '954 Patent by L'Oréal's customers, resellers, retailers, and end users by intentionally directing them and encouraging them to use, sell, and/or offer to sell within the United States and/or to import into the United States the Accused Products. L'Oréal provides written instructions, video tutorials, and otherwise instructs its customers how to use the Accused Products in an infringing manner. L'Oréal is liable for indirect infringement of the Asserted '954 Patent pursuant to 35 U.S.C. § 271(b).

137. Unless enjoined by this Court, L'Oréal will continue to infringe the Asserted '954 Patent and to actively induce others to infringe the Asserted '954 Patent, and Olaplex will continue to suffer irreparable harm for which there is no adequate remedy at law. Accordingly, Olaplex is entitled to preliminary and permanent injunctive relief against such infringement pursuant to 35 U.S.C. § 283.

138. As a direct and proximate result of L'Oréal's infringement, Olaplex has been and continues to be irreparably injured in its business and property rights, and is entitled to appropriate relief and to recover damages for such injuries pursuant to 35 U.S.C. § 284 in an amount to be proven at trial.

THIRD CAUSE OF ACTION

(Misappropriation of Trade Secrets Under the Defend Trade Secrets Act)

139. Olaplex realleges and incorporates herein by reference the allegations contained in the preceding paragraphs.

140. Olaplex owns the trade secrets described more fully in paragraphs 45 – 55 (hereafter "Olaplex Trade Secrets"), which give Olaplex a significant competitive advantage over would-be competitors, including L'Oréal. This advantage was compromised as a result of L'Oréal's unlawful activities.

141. Olaplex invested substantial resources to develop the Olaplex Trade Secrets, which derive independent economic value from not being generally known to the public or to other persons who can obtain economic value from their disclosure or use.

142. Olaplex made reasonable efforts under the circumstances to maintain the confidentiality of its trade secrets. Olaplex's efforts included, but are not limited to, (i) limiting the circulation of said materials within Olaplex; and (ii) protecting, limiting, and controlling access to Olaplex properties with physical or electronic means.

143. Olaplex did not consent to the use of any of the Olaplex Trade Secrets by anyone other than authorized individuals using them for Olaplex's own business purposes.

144. L'Oréal has illegally obtained and used Olaplex Trade Secrets as set forth above and through other means of which Olaplex presently is unaware.

145. On information and belief, at all times L'Oréal knew or had reason to know that Olaplex Trade Secrets were obtained from Olaplex by improper means.

146. On information and belief, L'Oréal has used and disclosed Olaplex Trade Secrets without Olaplex's consent and without regard to Olaplex's rights, and without compensation, permission, or licenses for the benefit of themselves and others. More specifically, L'Oréal has used these trade secrets in developing, marketing, and selling the Accused Products. Defendants' marketing and sale of the Accused Products continues to the present day, meaning that Defendants' trade secret misappropriation continues to the present day. Upon information and belief, Defendants are also continuing to further develop (*i.e.* improve) the Accused Product, and thus their use of Olaplex's trade secrets in product development also continues to the present day.

147. As set forth in paragraphs 77-85, L'Oréal's conduct was, is, and remains willful and wanton, and was taken with blatant disregard for Olaplex's valid and enforceable rights.

148. L'Oréal's wrongful conduct has caused and, unless enjoined by this Court, will continue in the future to cause irreparable injury to Olaplex. Olaplex has no adequate remedy at law for such wrongs and injuries. Moreover, paragraph 15 of the NDA executed by the parties expressly provides that "money damages would not be a sufficient remedy for any breach," and that the non-breaching party "shall . . . be entitled to equity relief, including, without limitation, injunction or specific performance." Olaplex is therefore entitled to an injunction restraining

and enjoining L'Oréal and its agents, servants, officers, directors, and employees, and all persons acting there under, in concert with, or on their behalf, from further using in any manner Olaplex Trade Secrets.

149. In addition, as a proximate result of L'Oréal's misconduct, Olaplex has suffered actual damages, and L'Oréal has been unjustly enriched. Specifically, L'Oréal used Olaplex's trade secrets to gain an unfair advantage in the bond-building and bleach-protection markets, and the erosion of Olaplex's market-share position is a direct result of L'Oréal's trade secret misappropriation.

150. L'Oréal's misappropriation of Olaplex Trade Secrets was willful and malicious; on information and belief, L'Oréal misappropriated Olaplex's Trade Secrets with the deliberate intent to injure Olaplex's business and improve its own. Olaplex is therefore entitled to enhanced damages and reasonable attorneys' fees.

FOURTH CAUSE OF ACTION
(MISAPPROPRIATION OF TRADE SECRETS UNDER DELAWARE TRADE SECRETS ACT)

151. Olaplex realleges and incorporates herein by reference the allegations contained in the preceding paragraphs.

152. The Olaplex Trade Secrets gave Olaplex a significant competitive advantage over would-be competitors, including L'Oréal. This advantage was compromised as a result of L'Oréal's unlawful activities.

153. Olaplex invested substantial resources to develop the Olaplex Trade Secrets, which derive independent economic value from not being generally known to the public or to other persons who can obtain economic value from their disclosure or use.

154. Olaplex made reasonable efforts under the circumstances to maintain the confidentiality of its trade secrets. Olaplex's efforts included, but are not limited to, (i) limiting the circulation of said materials within Olaplex; and (ii)

protecting, limiting, and controlling access to Olaplex properties with physical or electronic means.

155. Olaplex did not consent to the use of any of the Olaplex Trade Secrets by anyone other than authorized individuals using them for Olaplex's own business purposes.

156. L'Oréal has illegally obtained and used Olaplex Trade Secrets as set forth above and through other means of which Olaplex presently is unaware.

157. On information and belief, at all times L'Oréal knew or had reason to know that Olaplex Trade Secrets were obtained from Olaplex by improper means.

158. On information and belief, L'Oréal has used and disclosed Olaplex Trade Secrets without Olaplex's consent and without regard to Olaplex's rights, and without compensation, permission, or licenses for the benefit of themselves and others. More specifically, L'Oréal has used these trade secrets in developing, marketing, and selling the Accused Products. L'Oréal's marketing and sale of the Accused Products continues, such that Defendants' trade secret misappropriation continues to the present day. Upon information and belief, L'Oréal is also continuing to further develop (*i.e.* improve) the Accused Product, and thus its use of Olaplex's trade secrets in product development also continues to the present day.

159. L'Oréal's conduct was, is, and remains willful and wanton, and was taken with blatant disregard for Olaplex's valid and enforceable rights.

160. L'Oréal's wrongful conduct has caused and, unless enjoined by this Court, will continue in the future to cause irreparable injury to Olaplex. Olaplex has no adequate remedy at law for such wrongs and injuries. Olaplex is therefore entitled to an injunction restraining and enjoining L'Oréal and its agents, servants, officers, directors, and employees, and all persons acting there under, in concert with, or on their behalf, from further using in any manner Olaplex Trade Secrets.

161. In addition, as a proximate result of L'Oréal's misconduct, Olaplex has suffered actual damages, and L'Oréal has been unjustly enriched. Specifically, L'Oréal used Olaplex's trade secrets to gain an unfair advantage in the bond-building and bleach-protection markets, and the erosion of Olaplex's market-share position is a direct result of L'Oréal's trade secret misappropriation.

162. L'Oréal's misappropriation of Olaplex Trade Secrets was willful and malicious; on information and belief, L'Oréal misappropriated Olaplex's Trade Secrets with the deliberate intent to injure Olaplex's business and improve its own. Olaplex is therefore entitled to enhanced damages and reasonable attorneys' fees.

FIFTH CAUSE OF ACTION

(Breach of Contract)

163. Olaplex realleges and incorporates herein by reference the allegations contained in the preceding paragraphs.

164. Olaplex and L'Oréal USA, Inc., entered into a non-disclosure agreement, described herein and attached hereto as Exhibit C.

165. L'Oréal USA, Inc., breached the agreement by using Olaplex's confidential information for its own pecuniary gain, and also by disclosing Olaplex's confidential information to other co-defendants.

166. Olaplex was harmed by these breaches in an amount to be proven at trial. This harm includes the erosion of Olaplex's market-leading position in the market for hair bond building and bleach protection products. In violation of the non-disclosure agreement, L'Oréal used Olaplex's confidential information to gain an unfair advantage in this market, and the erosion of Olaplex's market-share position is a direct result of these contractual breaches.

167. Olaplex has been and will be further harmed irreparably as a result of L'Oréal's continued violations of the non-disclosure agreement, unless that conduct is enjoined by this Court.

PRAYER FOR RELIEF

WHEREFORE, Liqwd and Olaplex pray for entry of judgment against L'Oréal, as follows:

A. That L'Oréal has infringed, and/or induced the infringement of one or more claims of the Asserted Patents;

B. That L'Oréal has willfully infringed, and is willfully infringing the Asserted Patents;

C. That L'Oréal (including its parents, subsidiaries, affiliates, successors, predecessors, assigns, and the officers, directors, agents, servants, and employees of each of the foregoing, customers and/or licensees and those persons acting in concert or participation with any of them) be preliminarily and permanently enjoined and restrained under 35 U.S.C. § 283 from continued infringement, including but not limited to using, making, importing, offering for sale and/or selling products (such as the Accused Products) that infringe, and/or inducing the infringement of the Asserted Patents prior to their expiration;

D. That Olaplex be awarded damages, in accordance with 35 U.S.C. § 284, adequate to compensate it for the infringement that has occurred, but in no event less than a reasonable royalty for the use made of the inventions by L'Oréal, together with costs fixed by the Court;

E. An accounting and/or supplemental damages for all damages occurring after any discovery cutoff and through the Court's decision regarding the imposition of a permanent injunction;

F. That this case is found to be an exceptional case, that Olaplex be awarded treble damages due to L'Oréal's deliberate and willful conduct, and that L'Oréal is ordered to pay Olaplex's costs of suit and attorneys' fees as provided for by 35 U.S.C. § 285;

G. That Olaplex be granted prejudgment and post-judgment interest;

H. That Olaplex be awarded damages as a result of L'Oréal's trade secret misappropriation, and enhanced damages due to L'Oréal's willful and malicious conduct;

I. That L'Oréal (including its parents, subsidiaries, affiliates, successors, predecessors, assigns, and the officers, directors, agents, servants, and employees of each of the foregoing, customers and/or licensees and those persons acting in concert or participation with any of them) be preliminarily and permanently enjoined and restrained from further use of Olaplex's trade secrets, including but not limited to using, making, importing, offering for sale and/or selling products (such as the Accused Products) anywhere in the world.

K. That Olaplex be awarded its costs and expenses in this action, including, but not limited to, pursuant to paragraph 15 of the NDA, which states that the prevailing party shall be entitled to attorney's fees and costs;

L. That pursuant to paragraph 15 of the NDA, L'Oréal USA, Inc. agreed that money damages would not be sufficient remedy for any breach of the NDA and the non-breaching party shall, in connection with any determination that a breach has occurred, be entitled to equitable relief, including, without limitation, injunction or specific performance as a remedy for such breach, and consequently, L'Oréal USA, Inc. (including its parents, subsidiaries, affiliates, successors, predecessors, assigns, and the officers, directors, agents, servants, and employees of each of the foregoing, customers and/or licensees and those persons acting in concert or participation with any of them) be preliminarily and/or permanently enjoined and restrained from further use of Olaplex's confidential information, including but not limited to using, making, importing, offering for sale and/or selling products (such as the Accused Products) anywhere in the world; and

M. The Olaplex be granted such other and further relief as the Court deems just and appropriate, including monetary damages for all claims.

DEMAND FOR JURY TRIAL

Pursuant to Fed. R. Civ. P. 38(b), Olaplex demands a trial by jury on all issues triable by jury.

DATED: December 31, 2018

By:

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EXHIBIT A

US009498419B2

(12) **United States Patent**
Pressly et al.

(10) **Patent No.: US 9,498,419 B2**
(45) **Date of Patent: *Nov. 22, 2016**

(54) **KERATIN TREATMENT FORMULATIONS AND METHODS**

(71) Applicant: **Liqwd, Inc.**, Santa Barbara, CA (US)

(72) Inventors: **Eric D. Pressly**, Santa Barbara, CA (US); **Craig J. Hawker**, Santa Barbara, CA (US)

(73) Assignee: **Liqwd, Inc.**, Santa Barbara, CA (US)

(*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 0 days.

This patent is subject to a terminal disclaimer.

(21) Appl. No.: **15/087,415**

(22) Filed: **Mar. 31, 2016**

(65) **Prior Publication Data**

US 2016/0206535 A1 Jul. 21, 2016

Related U.S. Application Data

(63) Continuation of application No. 14/713,885, filed on May 15, 2015, now Pat. No. 9,326,926.

(60) Provisional application No. 61/994,709, filed on May 16, 2014.

(51) **Int. Cl.**

A61K 8/362	(2006.01)
A61Q 5/08	(2006.01)
A61Q 5/12	(2006.01)
A61Q 5/10	(2006.01)
A61K 8/41	(2006.01)
A45D 7/04	(2006.01)
A61Q 5/02	(2006.01)
A61Q 5/04	(2006.01)

(52) **U.S. Cl.**

CPC ***A61K 8/362*** (2013.01); ***A45D 7/04*** (2013.01); ***A61K 8/416*** (2013.01); ***A61Q 5/02*** (2013.01); ***A61Q 5/08*** (2013.01); ***A61Q 5/10*** (2013.01); ***A61Q 5/12*** (2013.01); *A61K 2800/591* (2013.01); *A61K 2800/882* (2013.01); *A61Q 5/04* (2013.01)

(58) **Field of Classification Search**

None

See application file for complete search history.

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(57) **ABSTRACT**

Formulations, kits, and methods for rebuilding the disulfide bonds in keratin found in hair, skin, or nails. Hair that is damaged due to a hair coloring treatment and/or other reducing treatment, such as during a permanent wave, can be treated with the formulations containing one or more active agents. The formulations may be applied subsequent to a hair coloring treatment or simultaneously with a hair coloring treatment. Use of the active agent formulations during a permanent wave treatment prevents the reversion of the hair to its previous state, for at least one week, preferably at least three months, more preferably at least one year, most preferably greater than one year, after one or more than one application of the formulation. Application of the active agent formulation to skin or nails can help repair damaged disulfide bonds due to natural wear and tear or natural aging.

10 Claims, No Drawings

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KERATIN TREATMENT FORMULATIONS AND METHODS

CROSS-REFERENCE TO RELATED APPLICATIONS

This application is a continuation of U.S. application Ser. No. 14/713,885, which claims benefit and priority to U.S. Provisional Application Ser. No. 61/994,709, filed May 16, 2014, the disclosures of which are incorporated herein by reference in its entirety.

FIELD OF THE INVENTION

The present invention generally relates to formulations and methods for treating keratin in hair, skin, or nails, and in particular for strengthening and/or repairing hair during or after a coloring or permanent wave treatment.

BACKGROUND OF THE INVENTION

Hair coloring is currently a globally accepted fashion phenomenon. Color treatments include hair coloring, highlighting, and bleaching. The coloring products can be categorized in several types, which include permanent, demi-permanent, semi-permanent, and temporary coloring formulations. Permanent hair coloring products make up the majority of the market worldwide.

Significant effort has been directed towards developing various approaches to hair dyeing; these include, oxidative dyes, direct action dyes, natural dyes, metallic dyes and reactive dyes. Many hair coloring formulations, in particular permanent coloring formulations, use reducing agents to break the disulfide bonds in the hair allowing deeper penetration of the hair coloring dyes and bleaching agents into the hair.

Disulfide bond linkages in hair are also broken by application of reducing agents, such as during permanent wave and hair straightening process. After the disulfide bonds are broken, the hair is placed in stress to establish the final style (e.g., straight, wavy, or curly), and the disulfide bonds are re-established.

Thioglycolic acid, particularly as the ammonium salt, is often used to cleave the cysteine disulfide bonds present in hair. Sodium bisulfite is another example of a known reducing agent commonly used in various dyes and bleaching agents in color treatments.

Typically, oxidation to restore the reduced bond is partially obtained when an oxidizing agent, such as hydrogen peroxide is present in a coloring formulation and/or by exposing the hair to atmospheric oxygen. However, this oxidation step can be very slow and can leave the hair frizzy and damaged.

Similarly, hair undergoing a permanent wave treatment is typically treated with a reducing agent followed by an oxidizing agent. Hydrogen peroxide is optionally added in a second step to restore the hair to its prior state. The newly formed disulfide bonds of the treated hair are under stress to maintain the hair's new shape; thus, they break easily resulting in a reversion of the hair style over time.

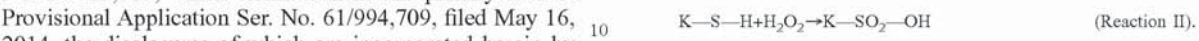
The use of peroxides in the hair styling process can result in damaged hair, removal of non-natural color from the hair, and/or leave the hair frizzy. Furthermore, some latent reduced thiols may remain in the hair even after oxidative

treatment. Hair styling treatments with peroxides involve the following reaction with thiol groups:

$$2K—S—H+H_2O_2 \rightarrow K—S—S—K+2H_2O \quad \text{(Reaction I)}$$

where K represents keratin in the hair.

In the case where two K—S—H groups are not present for Reaction I to take place, it is believed that the following reaction takes place, which results in damaged hair:



$$K—S—H+H_2O_2 \rightarrow K—SO_2—OH \quad \text{(Reaction II).}$$

In addition to being a major component in hair, keratin is also a major component in skin and nails. There are a number of different types of keratin and they are generally grouped as soft or hard keratins. Soft keratins are more prevalent in skin, while hard keratins predominate in hair and nails. Nails, in particular, are made of a modified keratin similar to that found hair. The disulfide bonds of the keratin in nails contribute to their impermeability. Therefore, damage to the disulfide bridges of keratin present in skin or nails can result in unhealthy and/or flaky skin or nails. Maintaining the disulfide bridges of keratin therefore helps to keep skin healthy and prevents cracking and splitting in nails.

Substantial improvement is needed in the areas of color saturation, color development, precise initial color consistency, improved wash fastness, and improved hair conditioning when applying color treatments. For example, the attainment of precise initial colors that are retained by the hair for a desirable time period has remained an elusive goal. The coloring formulations also cause severe hair damage, especially when coloring treatments are repeated. Moreover, various standard daily actions to the hair, for example hair brushing, hair blow-drying, and sun light exposure can cause even more damage to the hair.

Similar damage to the hair can also result from permanent wave treatments. In both coloring and permanent wave processes, improvements are also needed to repair damage and/or to strengthen the hair during or after such styling treatments. Additionally, improved treatments and methods are needed which can be applied to skin and nails to repair damaged keratin.

There is a need for hair formulations and treatments that repair and/or strengthen keratin in hair damaged from coloring and/or permanent wave treatments using reducing treatments.

There is also a need for hair formulations and treatments that can repair latent reduced thiols present in hair.

There is also a need for formulations and treatments that can repair damage to keratin present in skin and hair.

Therefore, it is an object of this invention to provide improved formulations and methods for repairing and/or strengthening damaged hair.

It is also an object of this invention to provide methods for using formulations that repair and/or strengthen hair after and/or during coloring or permanent wavetreatments.

It is also an object of this invention to provide formulations and methods for using these formulations to repair and/or strengthen hair after a reducing treatment.

It is also an object of this invention to provide formulations and methods for using these formulations that repair and/or strengthen keratin in hair, skin or nails due to natural wear and tear or due to natural aging.

SUMMARY OF THE INVENTION

Formulations, kits, and methods for restoring hair that has been broken during a hair coloring or permanent wave treatment are disclosed. The formulations have similar ben-

efits when used with different color chemical processes, such as bleaching, highlights, lowlights, semi-permanent, demi-permanent, and permanent color. Improved methods of styling hair, for example permanent hair waving and hair curling are also provided. The formulations can be applied each time the hair is washed or daily, once-weekly, twice-weekly, biweekly, once-monthly, every other month, or at less frequent intervals. Preferably, the formulations are applied once-monthly to achieve the desired results.

Traditional methods of permanent hair waving, hair curling, or straightening use hydrogen peroxide after a reducing treatment. The process generally takes about three days to complete. The methods disclosed herein use active agents to repair the hair; these active agents are washed from the individual's hair on the same day that they are applied to the hair. Under the same conditions, such as temperature and moisture, hair treated with the formulations disclosed herein takes a longer time to revert to its prior state as compared to the same hair that is treated with hydrogen peroxide.

The formulations disclosed herein contain one or more polyfunctional compounds. The polyfunctional compound contains at least one ionizable functional group capable of forming ionic bonds, and the polyfunctional compound also contains at least one functional group capable of forming a covalent bond with a thiol group. In some embodiments, the polyfunctional compounds contains at least two ionizable groups. Optionally, the formulation is applied at the same time as the hair coloring or permanent wave treatment. Alternatively, the formulation may be applied after the hair coloring or permanent wave treatment or to damaged hair. For example, the formulations can be applied within one week of the hair being treated and/or damaged, preferably within three days, more preferably within two days, most preferably immediately after application of the coloring or permanent wave treatment.

DETAILED DESCRIPTION OF THE INVENTION

I. Definitions

The term "hair" refers to one or more than one strand of hair, as well as the natural components of hair, such as oil from a body. Hair also refers to virgin hair or processed hair, for example hair that has been exposed to hair waving or hair straightening formulations.

"Pharmaceutically acceptable" and "cosmetically acceptable" are used interchangeably and refer to those compounds, materials, and/or formulations, which are, within the scope of sound medical judgment, suitable for use in contact with the tissues of human beings and animals without excessive toxicity, irritation, allergic response, or other problems or complications commensurate with a reasonable benefit/risk ratio. More specifically, pharmaceutically acceptable refers to a material, compound, or formulation that is suitable for use in contact with the skin, scalp, or hair. Pharmaceutically acceptable materials are known to those of ordinary skill in the art.

"Shampoo", as used herein, generally refers to a liquid or semi-solid formulation applied to hair that contains detergent or soap for washing the hair.

"Conditioner", as used herein, generally refers to a formulation (e.g., liquid, cream, lotion, gel, semi-solid) applied to hair to soften the hair, smooth the hair, and/or change the sheen of the hair.

"Analog" and "derivative" are used herein interchangeably, and refer to a compound that possesses the same core as the parent compound, but differs from the parent compound in bond order, the absence or presence of one or more atoms and/or groups of atoms, or a combination thereof. The derivative can differ from the parent compound, for example, in one or more substituents present on the core, which may include one or more atoms, functional groups, or substructures. In general, a derivative can be formed, at least theoretically, from the parent compound via chemical and/or physical processes.

"Electrophilic group" or "electrophilic moiety" are used interchangeably and refer to one or more functional groups or moieties that have an affinity for or attract electrons.

"Nucleophilic group" or "nucleophilic moiety" are used interchangeably and refer to one or more functional groups or moieties that are electron rich and are capable of reacting with electrophilic groups.

"Michael acceptor", as used herein, is a species of electrophilic groups or moieties that participates in nucleophilic addition reactions. The Michael acceptor can be or can contain an α,β-unsaturated carbonyl-containing group or moiety, such as a ketone. Other Michael acceptors include pi-bonds, such as double or triple bonds conjugated to other pi-bond containing electron withdrawing groups, such as nitro groups, nitrile groups, and carboxylic acid groups.

"Carboxylic acid," as used in here refers to the group —COOH. Unless specified otherwise the term carboxylic acid embraces both the free acid and carboxylate salt.

"Alkyl", as used herein, refers to the radical of saturated or unsaturated aliphatic groups, including straight-chain alkyl, alkenyl, or alkynyl groups, branched-chain alkyl, alkenyl, or alkynyl groups, cycloalkyl, cycloalkenyl, or cycloalkynyl (alicyclic) groups, alkyl substituted cycloalkyl, cycloalkenyl, or cycloalkynyl groups, and cycloalkyl substituted alkyl, alkenyl, or alkynyl groups. Unless otherwise indicated, a straight chain or branched chain alkyl has 30 or fewer carbon atoms in its backbone (e.g., C_1-C_{30} for straight chain, C_3-C_{30} for branched chain), more preferably 20 or fewer carbon atoms, more preferably 12 or fewer carbon atoms, and most preferably 8 or fewer carbon atoms. In some embodiments, the chain has 1-6 carbons. Likewise, preferred cycloalkyls have from 3-10 carbon atoms in their ring structure, and more preferably have 5, 6 or 7 carbons in the ring structure. The ranges provided above are inclusive of all values between the minimum value and the maximum value.

The term "alkyl" includes both "unsubstituted alkyls" and "substituted alkyls", the latter of which refers to alkyl moieties having one or more substituents replacing a hydrogen on one or more carbons of the hydrocarbon backbone. Such substituents include, but are not limited to, halogen, hydroxyl, carbonyl (such as a carboxyl, alkoxycarbonyl, formyl, or an acyl), thiocarbonyl (such as a thioester, a thioacetate, or a thioformate), alkoxyl, phosphoryl, phosphate, phosphonate, a phosphinate, amino, amido, amidine, imine, cyano, nitro, azido, sulfhydryl, alkylthio, sulfate, sulfonate, sulfamoyl, sulfonamido, sulfonyl, heterocyclyl, aralkyl, or an aromatic or heteroaromatic moiety.

Unless the number of carbons is otherwise specified, "lower alkyl" as used herein means an alkyl group, as defined above, but having from one to ten carbons, more preferably from one to six carbon atoms, in its backbone structure. Likewise, "lower alkenyl" and "lower alkynyl" have similar chain lengths. Preferred alkyl groups are lower alkyls.

The alkyl groups may also contain one or more heteroatoms within the carbon backbone. Examples include oxygen,

nitrogen, sulfur, and combinations thereof. In certain embodiments, the alkyl group contains between one and four heteroatoms.

"Alkenyl" and "Alkynyl", as used herein, refer to unsaturated aliphatic groups containing one or more double or triple bonds analogous in length (e.g., C_2-C_{30}) and possible substitution to the alkyl groups described above.

"Aryl", as used herein, refers to 5-, 6- and 7-membered aromatic rings. The ring may be a carbocyclic, heterocyclic, fused carbocyclic, fused heterocyclic, bicarbocyclic, or biheterocyclic ring system, optionally substituted as described above for alkyl. Broadly defined, "Ar", as used herein, includes 5-, 6- and 7-membered single-ring aromatic groups that may include from zero to four heteroatoms. Examples include, but are not limited to, benzene, pyrrole, furan, thiophene, imidazole, oxazole, thiazole, triazole, pyrazole, pyridine, pyrazine, pyridazine and pyrimidine. Those aryl groups having heteroatoms in the ring structure may also be referred to as "heteroaryl", "aryl heterocycles", or "heteroaromatics". The aromatic ring can be substituted at one or more ring positions with such substituents as described above, for example, halogen, azide, alkyl, aralkyl, alkenyl, alkynyl, cycloalkyl, hydroxyl, alkoxyl, amino, nitro, sulfhydryl, imino, amido, phosphonate, phosphinate, carbonyl, carboxyl, silyl, ether, alkylthio, sulfonyl, sulfonamido, ketone, aldehyde, ester, heterocyclyl, aromatic or heteroaromatic moieties, —CF_3, and —CN. The term "Ar" also includes polycyclic ring systems having two or more cyclic rings in which two or more carbons are common to two adjoining rings (the rings are "fused rings") wherein at least one of the rings is aromatic, e.g., the other cyclic rings can be cycloalkyls, cycloalkenyls, cycloalkynyls, aryls and/or heterocycles, or both rings are aromatic.

"Alkylaryl", as used herein, refers to an alkyl group substituted with an aryl group (e.g., an aromatic or hetero aromatic group).

"Heterocycle" or "heterocyclic", as used herein, refers to a cyclic radical attached via a ring carbon or nitrogen of a monocyclic or bicyclic ring containing 3-10 ring atoms, and preferably from 5-6 ring atoms, containing carbon and one to four heteroatoms each selected from non-peroxide oxygen, sulfur, and N(Y) wherein Y is absent or is H, O, (C_{1-4}) alkyl, phenyl or benzyl, and optionally containing one or more double or triple bonds, and optionally substituted with one or more substituents. The term "heterocycle" also encompasses substituted and unsubstituted heteroaryl rings. Examples of heterocyclic ring include, but are not limited to, benzimidazolyl, benzofuranyl, benzothiofuranyl, benzothiophenyl, benzoxazolyl, benzoxazolinyl, benzthiazolyl, benztriazolyl, benztetrazolyl, benzisoxazolyl, benzisothiazolyl, benzimidazolinyl, carbazolyl, 4aH-carbazolyl, carbolinyl, chromanyl, chromenyl, cinnolinyl, decahydroquinolinyl, 2H,6H-1,5,2-dithiazinyl, dihydrofuro[2,3-b]tetrahydrofuran, furanyl, furazanyl, imidazolidinyl, imidazolinyl, imidazolyl, 1H-indazolyl, indolenyl, indolinyl, indolizinyl, indolyl, 3H-indolyl, isatinoyl, isobenzofuranyl, isochromanyl, isoindazolyl, isoindolinyl, isoindolyl, isoquinolinyl, isothiazolyl, isoxazolyl, methylenedioxyphenyl, morpholinyl, naphthyridinyl, octahydroisoquinolinyl, oxadiazolyl, 1,2,3-oxadiazolyl, 1,2,4-oxadiazolyl, 1,2,5-oxadiazolyl, 1,3,4-oxadiazolyl, oxazolidinyl, oxazolyl, oxindolyl, pyrimidinyl, phenanthridinyl, phenanthrolinyl, phenazinyl, phenothiazinyl, phenoxathinyl, phenoxazinyl, phthalazinyl, piperazinyl, piperidinyl, piperidonyl, 4-piperidonyl, piperonyl, pteridinyl, purinyl, pyranyl, pyrazinyl, pyrazolidinyl, pyrazolinyl, pyrazolyl, pyridazinyl, pyridooxazole, pyridoimidazole, pyridothiazole, pyridinyl, pyridyl, pyrimidinyl, pyrrolidinyl, pyrrolinyl, 2H-pyrrolyl, pyrrolyl, quinazolinyl, quinolinyl, 4H-quinolizinyl, quinoxalinyl, quinuclidinyl, tetrahydrofuranyl, tetrahydroisoquinolinyl, tetrahydroquinolinyl, tetrazolyl, 6H-1,2,5-thiadiazinyl, 1,2,3-thiadiazolyl, 1,2,4-thiadiazolyl, 1,2,5-thiadiazolyl, 1,3,4-thiadiazolyl, thianthrenyl, thiazolyl, thienyl, thienothiazolyl, thienooxazolyl, thienoimidazolyl, thiophenyl and xanthenyl.

"Heteroaryl", as used herein, refers to a monocyclic aromatic ring containing five or six ring atoms containing carbon and 1, 2, 3, or 4 heteroatoms each selected from non-peroxide oxygen, sulfur, and N(Y) where Y is absent or is H, O, (C_1-C_8) alkyl, phenyl or benzyl. Non-limiting examples of heteroaryl groups include furyl, imidazolyl, triazolyl, triazinyl, oxazoyl, isoxazoyl, thiazolyl, isothiazoyl, pyrazolyl, pyrrolyl, pyrazinyl, tetrazolyl, pyridyl, (or its N-oxide), thienyl, pyrimidinyl (or its N-oxide), indolyl, isoquinolyl (or its N-oxide), quinolyl (or its N-oxide) and the like. The term "heteroaryl" can include radicals of an ortho-fused bicyclic heterocycle of about eight to ten ring atoms derived therefrom, particularly a benz-derivative or one derived by fusing a propylene, trimethylene, or tetramethylene diradical thereto. Examples of heteroaryl include, but are not limited to, furyl, imidazolyl, triazolyl, triazinyl, oxazoyl, isoxazoyl, thiazolyl, isothiazoyl, pyraxolyl, pyrrolyl, pyrazinyl, tetrazolyl, pyridyl (or its N-oxide), thientyl, pyrimidinyl (or its N-oxide), indolyl, isoquinolyl (or its N-oxide), quinolyl (or its N-oxide), and the like.

"Halogen", as used herein, refers to fluorine, chlorine, bromine, or iodine.

The term "substituted," as used herein, refers to all permissible substituents of the compounds described herein. In the broadest sense, the permissible substituents include acyclic and cyclic, branched and unbranched, carbocyclic and heterocyclic, aromatic and nonaromatic substituents of organic compounds. Illustrative substituents include, but are not limited to, halogens, hydroxyl groups, or any other organic groupings containing any number of carbon atoms, preferably 1-14 carbon atoms, and optionally include one or more heteroatoms such as oxygen, sulfur, or nitrogen grouping in linear, branched, or cyclic structural formats. Representative substituents include alkyl, substituted alkyl, alkenyl, substituted alkenyl, alkynyl, substituted alkynyl, phenyl, substituted phenyl, aryl, substituted aryl, heteroaryl, substituted heteroaryl, halo, hydroxyl, alkoxy, substituted alkoxy, phenoxy, substituted phenoxy, aroxy, substituted aroxy, alkylthio, substituted alkylthio, phenylthio, substituted phenylthio, arylthio, substituted arylthio, cyano, isocyano, substituted isocyano, carbonyl, substituted carbonyl, carboxyl, substituted carboxyl, amino, substituted amino, amido, substituted amido, sulfonyl, substituted sulfonyl, sulfonic acid, phosphoryl, substituted phosphoryl, phosphonyl, substituted phosphonyl, polyaryl, substituted polyaryl, C_3-C_{20} cyclic, substituted C_3-C_{20} cyclic, heterocyclic, substituted heterocyclic, aminoacid, peptide, and polypeptide groups.

Heteroatoms, such as nitrogen, may have hydrogen substituents and/or any permissible substituents of organic compounds described herein that satisfy the valences of the heteroatoms. It is understood that "substitution" or "substituted" includes the implicit proviso that such substitution is in accordance with permitted valence of the substituted atom and the substituent, and that the substitution results in a stable compound, i.e. a compound that does not spontaneously undergo transformation such as by rearrangement, cyclization, elimination, etc.

"Polymer", as used herein, refers to a molecule containing more than 10 monomer units.

"Water-soluble", as used herein, generally means at least 50, 75, 100, 125, 150, 200, 225, or 250 g is soluble in 1 L of water at 25° C.

II. Formulations

The formulations and methods disclosed herein are concerned with treating keratin in hair, skin, or nails. In one embodiment, the methods relate to strengthening and/or repairing hair after it has undergone a coloring treatment or after or during a permanent wave treatment. Additionally, the formulations may reduce or prevent hair damage due to hair coloring and/or bleaching processes.

A. Formulations

The formulations contain one or more polyfunctional compounds (also referred to herein as "active agents").

The active agents can be combined with one or more pharmaceutically acceptable carriers and/or excipients that are considered safe and effective to human hair and/or human scalp, and may be administered to an individual's hair without causing undesirable biological side effects, such as burning, itching, and/or redness, or similar adverse reactions. The formulations may further contain an excipient that renders the formulations neutral pH, or a pH ranging from about pH 3 to about pH 12, preferably from pH 5 to pH 8.

The active agent is typically present in an amount ranging from about 0.01 wt % to about 50 wt % of the formulation, preferably from about from about 1 wt % to about 25 wt % of the formulation, more preferably from about 1 wt % to about 15 wt %, most preferably from about 1 wt % to about 10 wt %. Typically, the active agent may be present in an amount ranging from about 0.5 to about 3 wt % of the formulation, or from about 1 to about 3 wt % of the formulation.

The active agent is stable in aqueous solution for a period of at least 2, 3, 4, 5, 6, 8, 9, 10, 11, or 12 months or longer at pH of 6 to 8 and a temperature of about 25-30° C., preferably about 25° C. "Stable" as used herein with respect to shelf-life means that at least 40, 45, 50, 55, 60, 65, 70, 75, 80, 85, 90, or 95% of the compound is unchanged over the specified period.

a. Active Agents

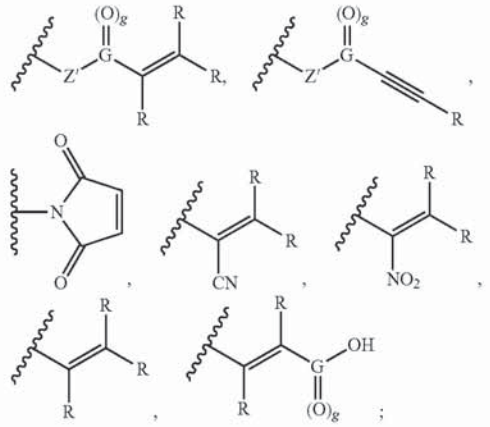
The active agent is a polyfunctional compound that may contain ionizable functional groups capable of forming ionic bonds and functional groups capable of forming a covalent bond with a thiol. Suitable ionizable functional groups include, but are not limited to, acidic groups such as carboxylic acids, sulfonic acids, phosphonic acids, and basic groups, such as amines. Suitable functional groups capable of forming a covalent bond with a thiol include, but are not limited to, Michael acceptors, alkyl halides or sulfonate esters.

The active agent may have the following Formula I:

$$(B)_m—Z-(A)_n \qquad \text{Formula I}$$

wherein Z is a linker or is absent, m and n are each an integer independently selected from 0-6, provided that m+n is at least 2, B is a functional group capable of forming a covalent bond with a thiol, and A is an ionizable functional group. In some embodiments, ionizable group A can be independently selected from the group consisting of: —COOH, —SO_3H, —PO_3H_2, and —$N(R^1)_2$; wherein R^1 is independently selected from the group consisting of a hydrogen, alkyl, alkenyl, alkynyl, cycloalkyl, aryl, heterocycloalkyl and heteroaryl groups; wherein each R^1 is independently unsubstituted or substituted with one or more substituents. In some other embodiments, ionizable group A can be an ionic group, such as —$N^+(R^1)_3$. In some preferred embodiments, each R^1 is independently selected from a methyl, ethyl, or isopropyl group.

Exemplary active agents according to Formula I may contain thiol reactive functional groups, as group B, for example, such as those shown in the following moieties:



wherein R is independently selected from hydrogen, C_{1-6} alkyl, aryl, or an ionizable functional group; Z' is oxygen (O), NH, or is absent; and G is carbon (C) and g is 1, or G is sulfur (S) and g is 2.

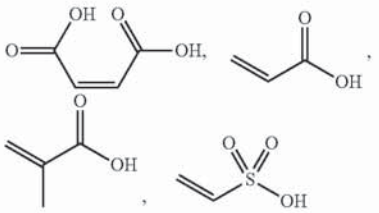
The linker Z, when present, can be or can contain an alkyl, alkenyl, cycloalkyl, cycloalkenyl, aryl, heterocycloalkyl or heteroaryl group. One or more of the carbon atoms in the alkyl, alkenyl, cycloalkyl, cycloalkenyl, and aryl groups can be substituted with a heteroatom, yielding, for instance, an ether or alkylamine-containing linker.

The linker Z may optionally be substituted with one or more substituents, which may be the same or different, including hydrogen, halogen, cyano, alkoxy, alkyl, alkenyl, cycloalkyl, cycloalkenyl, aryl, heterocycloalkyl, heteroaryl, amine, hydroxy, oxo, formyl, acyl, carboxylic acid (—COOH), —$C(O)R^1$, —$C(O)OR^1$, carboxylate (—COO—), primary amide (e.g., —$CONH_2$), secondary amide (e.g., —$CONHR_{11}$), —$C(O)NR^1R^2$, —NR^1R^2, —$NR^1S(O)_2R^2$, —$NR^1C(O)R^2$, —$S(O)_2R^2$, —SR^1, and —$S(O)_2NR^1R^2$, sulfonyl group (e.g., —SOR_1), and sulfonyl group (e.g., —$SOOR_1$); wherein R^1 and R^2 may each independently be hydrogen, alkyl, alkenyl, alkynyl, cycloalkyl, aryl, heterocycloalkyl and heteroaryl; wherein each of R^1 and R^2 is optionally independently substituted with one or more substituents selected from the group consisting of halogen, hydroxyl, oxo, cyano, nitro, amino, alkylamino, dialkylamino, alkyl optionally substituted with one or more halogen or alkoxy or aryloxy, aryl optionally substituted with one or more halogen or alkoxy or alkyl or trihaloalkyl, heterocycloalkyl optionally substituted with aryl or heteroaryl or oxo or alkyl optionally substituted with hydroxyl, cycloalkyl optionally substituted with hydroxyl, heteroaryl optionally substituted with one or more halogen or alkoxy or alkyl or trihaloalkyl, haloalkyl, hydroxyalkyl, carboxy, alkoxy, aryloxy, alkoxycarbonyl, aminocarbonyl, alkylaminocarbonyl and dialkylaminocarbonyl.

In certain preferred embodiments, the linker Z is a C_{1-10} alkyl group which may be unsubstituted or substituted one or more times by oxo, hydroxyl, carboxyl, amido or amino. Preferably, the linker Z is a C_{1-4} alkyl group. The alkyl group may be linear or branched. The alkyl group may also be

interrupted one or more times by a heteroatom selected from oxygen, sulfur and nitrogen. An example of such a dicarboxylic acids having a heteroatom interruption is thiodipropionic acid. In other embodiments, the alkyl group may contain one or more double or triple bonds.

In some embodiments, the active agent of Formula I has one of the following structures:



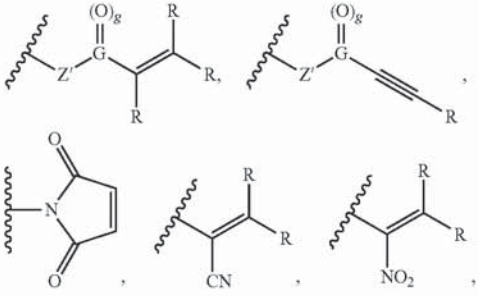
or is a simple salt of these structures.

In certain other embodiments, the active agent may have the following Formula II:

$$(B)_m—Z-(A)_n-(C)_o \qquad \text{Formula II}$$

wherein Z is a linker or is absent, m and n are each an integer independently selected from 0-6, provided that m+n is at least 2, B is a functional group capable of forming a covalent bond with a nucleophile, such as but not limited to a thiol or amine group, A is an ionizable functional group as defined above, and C contains an ionic group and a functional group which is also capable of forming a covalent bond with a nucleophile, such as but not limited to a thiol or amine group, and which has a charge opposite to that of ionizable group A. Group C is ionically bonded (denoted by dashed line) to group A. For ionic group C, o is an integer value independently selected from 0-6, such that the sum of charges of group C and ionizable group A is zero. In some embodiments, ionizable group A can be independently selected from the group consisting of: —COOH, —SO_3H, —PO_3H_2, and —$N(R^1)_2$; wherein R^1 is independently selected from the group consisting of a hydrogen, alkyl, alkenyl, alkynyl, cycloalkyl, aryl, heterocycloalkyl and heteroaryl groups; wherein each R^1 is independently unsubstituted or substituted with one or more substituents. In some other embodiments, ionizable group A can be an ionic group such as —$N^+(R^1)_3$. In some preferred embodiments, each R^1 is independently selected from a methyl, ethyl, or isopropyl group.

The active agents according to Formula II may contain thiol reactive functional groups as group B, for example, such as those shown in the following moieties:



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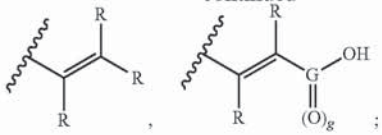


wherein R is independently selected from hydrogen, C_{1-6} alkyl, aryl, or an ionizable functional group; Z' is oxygen (O), NH, or is absent; and G is carbon (C) and g is 1, or G is sulfur (S) and g is 2.

The linker Z, when present, can be or can contain an alkyl, alkenyl, cycloalkyl, cycloalkenyl, aryl, heterocycloalkyl or heteroaryl group. One or more of the carbon atoms in the alkyl, alkenyl, cycloalkyl, cycloalkenyl, and aryl groups can be substituted with a heteroatom, yielding, for instance, an ether or alkylamine-containing linker.

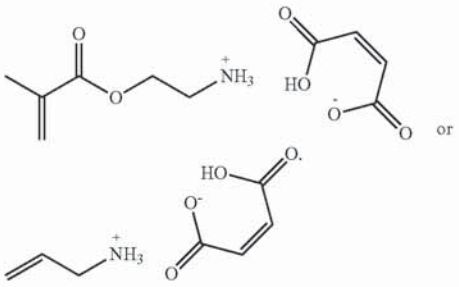
The linker Z may optionally be substituted with one or more substituents, which may be the same or different, including hydrogen, halogen, cyano, alkoxy, alkyl, alkenyl, cycloalkyl, cycloalkenyl, aryl, heterocycloalkyl, heteroaryl, amine, hydroxy, oxo, formyl, acyl, carboxylic acid (—COOH), —$C(O)R^1$, —$C(O)OR^1$, carboxylate (—COO—), primary amide (e.g., —$CONH_2$), secondary amide (e.g., —$CONHR^1$), —$C(O)NR^1R^2$, —NR^1R^2, —$NR^1S(O)_2R^2$, —$NR^1C(O)R^2$, —$S(O)_2R^2$, —SR^1, and —$S(O)_2NR^1R^2$, sulfinyl group (e.g., —SOR_1), and sulfonyl group (e.g., —$SOOR^1$); wherein R^1 and R^2 may each independently be hydrogen, alkyl, alkenyl, alkynyl, cycloalkyl, aryl, heterocycloalkyl and heteroaryl; wherein each of R^1 and R^2 is optionally independently substituted with one or more substituents selected from the group consisting of halogen, hydroxyl, oxo, cyano, nitro, amino, alkylamino, dialkylamino, alkyl optionally substituted with one or more halogen or alkoxy or aryloxy, aryl optionally substituted with one or more halogen or alkoxy or alkyl or trihaloalkyl, heterocycloalkyl optionally substituted with aryl or heteroaryl or oxo or alkyl optionally substituted with hydroxyl, cycloalkyl optionally substituted with hydroxyl, heteroaryl optionally substituted with one or more halogen or alkoxy or alkyl or trihaloalkyl, haloalkyl, hydroxyalkyl, carboxy, alkoxy, aryloxy, alkoxycarbonyl, aminocarbonyl, alkylaminocarbonyl and dialkylaminocarbonyl.

In certain preferred embodiments, the linker Z is a C_{1-10} alkyl group which may be unsubstituted or substituted one or more times by oxo, hydroxyl, carboxyl, amido or amino. Preferably, the linker Z is a C_{1-4} alkyl group. The alkyl group may be linear or branched. The alkyl group may also be interrupted one or more times by a heteroatom selected from oxygen, sulfur and nitrogen. An example of such a dicarboxylic acids having a heteroatom interruption is thiodipropionic acid. In other embodiments, the alkyl group may contain one or more double or triple bonds.

Group C is an ionic group ionically bonded to ionizable group A and contains at least one thiol reactive selected from a Michael acceptor, a succinimidyl-containing group, a maleimido-containing group, azlactone, a benzoxazinone derivative, vinyl sulfone, vinyl sulfoximine, vinyl sulfonate, vinyl phosphonate, benzoxazinone, isocyanate, epoxide, an electrophilic moiety containing a leaving group, an electrophilic thiol acceptor, acrylic or acrylate group, a methacrylic or methacrylate group, a styrene group, an acryl amide group, a methacryl amide group, a maleate group, a fumarate group, an itaconate group, a vinyl ether group, an allyl ether group, an allyl ester group, a vinyl ester group, a sulfonate group, a phosphonate group, a sulfoxide group, a sulfona-

mide group, a sulfinimide group, a sulfinamide group, a sulfonimidate group, or a sulfonimidamide group.

In some embodiments, the active agent of Formula II has one of the following structures:



b. Excipients

The formulations typically contain one or more cosmetically acceptable excipients. Cosmetically acceptable excipients include, but are not limited to preservatives, antioxidants, chelating agents, sunscreen agents, vitamins, dyes, hair coloring agents, proteins, amino acids, natural extracts such as plant extracts, humectants, fragrances, perfumes, oils, emollients, lubricants, butters, penetrants, thickeners, viscosity modifiers, polymers, resins, hair fixatives, film formers, surfactants, detergents, emulsifiers, opacifying agents, volatiles, propellants, liquid vehicles, carriers, salts, pH adjusting agents (e.g., citric acid), neutralizing agents, buffers, hair conditioning agents, anti-static agents, anti-frizz agents, anti-dandruff agents, absorbents, and combinations thereof.

The formulations typically contain at least two cosmetically acceptable excipients. In some forms, the formulations contain the active agent, water, and optionally a preservative and/or fragrance.

The formulation for treating hair may be in any suitable physical foul'. Suitable forms include, but are not limited to low to moderate viscosity liquids, lotions, milks, mousses, sprays, gels, creams, shampoos, conditioners, and the like. Suitable excipients, such as those listed above, are included or excluded from the hair care formulation depending on the form of use of the formulation (e.g., hair spray, cream, conditioner, or shampoo).

The pharmaceutical excipient is typically present in an amount ranging from about 10 wt % to about 99.99 wt % of the formulation, preferably about 40 wt % to about 99 wt %, more preferably from about 80 wt % to about to about 99 wt %.

i. Surfactants

Surfactants are surface-active agents that are able to reduce the surface tension of water and cause the hair formulation to slip across or onto the skin or hair. Surfactants also include detergents and soap. The surfactants may be amphoteric, anionic, or cationic. Suitable surfactants that may be used in the formulation include, but are not limited to, 3-aminopropane sulfonic acid, almond amide, almond amidopropyl betaine, almond amidopropylamine oxide, aluminum hydrogenated tallow glutamate, aluminum lanolate, aminoethyl sulfate, aminopropyl lauryl glutamine, ammonium C_{12-15} alkyl sulfate, ammonium C_{12-15} pareth sulfate, ammonium C_{12-16} alkyl sulfate, ammonium C_{9-10} perfluoroalkylsulfonate, ammonium capryleth sulfate, ammonium capryleth-3 sulfate, ammonium monoglyceride sulfate, ammonium sulfate, ammonium isothionate, ammonium cocoyl sarcosinate, ammonium cumene sulfonate, ammonium dimethicone copolyol sulfate, ammonium dodecylbenzenesulfonate, ammonium isostearate, ammonium laureth sulfate, ammonium laureth-12 sulfate, ammonium laureth-5 sulfate, ammonium laureth-6 carboxylate, ammonium laureth-7 sulfate, ammonium laureth-8 carboxylate, ammonium laureth-9 sulfate, ammonium lauroyl sarcosinate, ammonium lauryl sulfate, ammonium lauryl sulfosuccinate, ammonium myreth sulfate, ammonium myristyl sulfate, ammonium nonoxynol-30 sulfate, ammonium nonoxynol-4 sulfate, ammonium oleate, ammonium palm kernel sulfate, ammonium polyacrylate, ammonium stearate, ammonium tallate, ammonium xylene sulfonate, ammonium xylene sulfonate, amp-isostearoyl gelatin/keratin amino acids/lysine hydroxypropyltrimonium chloride, amp-isostearoyl hydrolyzed collagen, apricot kernel oil PEG-6 esters, apricot amide, apricot amidopropyl betaine, arachideth-20, avocadamide, avocadamidopropyl betaine, babassuamide, babassuamidopropyl betaine, babassuamidopropylamine oxide, behenalkonium chloride, behenamide, behenamide, behenamidopropyl betaine, behenamine oxide, sodium laureth sulfate, sodium lauryl sulfate, a polyoxyether of lauryl alcohol or ceteareth-20, or combinations thereof

Suitable anionic surfactants include, but are not limited to, those containing carboxylate, sulfonate and sulfate ions. Examples of anionic surfactants include sodium, potassium, ammonium of long chain alkyl sulfonates and alkyl aryl sulfonates such as sodium dodecylbenzene sulfonate; dialkyl sodium sulfosuccinates, such as sodium dodecylbenzene sulfonate; dialkyl sodium sulfosuccinates, such as sodium bis-(2-ethylthioxyl)-sulfosuccinate; and alkyl sulfates such as sodium lauryl sulfate. Cationic surfactants include, but are not limited to, quaternary ammonium compounds such as benzalkonium chloride, benzethonium chloride, cetrimonium bromide, stearyl dimethylbenzyl ammonium chloride, polyoxyethylene and coconut amine. Examples of nonionic surfactants include ethylene glycol monostearate, propylene glycol myristate, glyceryl monostearate, glyceryl stearate, polyglyceryl-4-oleate, sorbitan acylate, sucrose acylate, PEG-150 laurate, PEG-400 monolaurate, polyoxyethylene monolaurate, polysorbates, polyoxyethylene octylphenylether, PEG-1000 cetyl ether, polyoxyethylene tridecyl ether, polypropylene glycol butyl ether, Poloxamer® 401, stearoyl monoisopropanolamide, and polyoxyethylene hydrogenated tallow amide. Examples of amphoteric surfactants include sodium N-dodecyl-.beta.-alanine, sodium N-lauryl-β-iminodipropionate, myristoamphoacetate, lauryl betaine and lauryl sulfobetaine.

More than one surfactant may be included in the formulation.

The surfactants are optionally included in an amount ranging from about 0.1% to about 15% by weight of the formulation, preferably about 1% to about 10% by weight of the formulation.

ii. Emollients

Emollient refers to a material that protects against wetness or irritation, softens, soothes, coats, lubricates, moisturizes, protects, and/or cleanses the skin. Suitable emollients for use in the formulations include, but are not limited to, a silicone compound (e.g., dimethicone, cyclomethicone, dimethicone copolyol or a mixture of cyclopentasiloxane and dimethicone/vinyldimethicone cross polymer, cyclopentasiloxane polysilicone), polyols such as sorbitol, glycerin, propylene glycol, ethylene glycol, polyethylene glycol, caprylyl glycol, polypropylene glycol, 1,3-butane diol, hexylene glycol, isoprene glycol, xylitol; ethylhexyl palmitate; a triglyceride such as caprylic/capric triglyceride and fatty acid ester such as cetearyl isononanoate or cetyl palmitate. In a specific

embodiment, the emollient is dimethicone, amidodimethicone, dimethiconol, cyclopentasiloxane, potassium dimethicone PEG-7 panthenyl phosphate, or combinations thereof. More than one emollient may be included in the formulation.

The emollient is optionally included in an amount ranging from about 0.5% to about 15% by weight of the formulation, preferably from about 1% to about 10% by weight of the formulation.

iii. Emulsifiers

The formulation may also contain one or more emulsifiers. Suitable emulsifiers include, but are not limited to, copolymers of an unsaturated ester and styrene sulfonate monomer, cetearyl alcohol, glyceryl ester, polyoxyethylene glycol ether of cetearyl alcohol, stearic acid, polysorbate-20, ceteareth-20, lecithin, glycol stearate, polysorbate-60, polysorbate-80, or combinations thereof. More than one emulsifier may be included in the formulation.

The emulsifier is optionally included in an amount ranging from about 0.05%-15% by weight of the formulation, preferably from about 0.1%-10% by weight of the formulation.

iv. Preservatives

One or more preservatives may be included in the formulation. Suitable preservatives include, but are not limited to, glycerin containing compounds (e.g., glycerin or ethylhexylglycerin or phenoxyethanol), benzyl alcohol, parabens (methylparaben, ethylparaben, propylparaben, butylparaben, isobutylparaben, etc.), sodium benzoate, ethylenediamine-tetraacetic acid (EDTA), potassium sorbate, and/or grapefruit seed extract, or combinations thereof. More than one preservative may be included in the formulation. Other preservatives are known in the cosmetics industries and include salicylic acid, DMDM Hydantoin, Formaldahyde, Chlorphenism, Triclosan, Imidazolidinyl Urea, Diazolidinyl Urea, Sorbic Acid, Methylisothiazolinone, Sodium Dehydroacetate, Dehydroacetic Acid, Quaternium-15, Stearalkonium Chloride, Zinc Pyrithione, Sodium Metabisulfite, 2-Bromo-2-Nitropropane, Chlorhexidine Digluconate, Polyaminopropyl biguanide, Benzalkonium Chloride, Sodium Sulfite, Sodium Salicylate, Citric Acid, Neem Oil, Essential Oils (various), Lactic Acid, and Vitamin E (tocopherol).

The preservative is optionally included in an amount ranging from about 0.1% to about 5% by weight of the formulation, preferably from about 0.3% to about 3% by weight of the formulation. Preferably, the formulations are paraben free.

v. Conditioning Agents

One or more conditioning agents may be included in the formulation. Suitable conditioning agents include, but are not limited to, silicone-based agents (e.g., silicone quaternium-8), panthenol, hydrolyzed wheat and/or soy protein, amino acids (e.g. wheat amino acids), rice bran wax, meadowfoam seed oil, mango seed oil, grape seed oil, jojoba seed oil, sweet almond oil, hydroxyethyl behenamidopropyl dimonium chloride, aloe leaf extract, aloe barbadensis leaf juice, phytantriol, panthenol, retinyl palmitate, behentrimonium methosulfate, cyclopentasiloxane, quaternium-91, stearamidopropyl dimethylamine, and combinations thereof.

The conditioning agent(s) is optionally included in an amount ranging from about 0.1% to about 5% by weight of the formulation, preferably from about 0.3% to about 3% by weight of the formulation.

vi. Diluents

Diluent, as used herein, refers to a substance(s) that dilutes the active agent. Water is the preferred diluent. The formulation typically contains greater than one percent (by wt) water, preferably greater than five percent (by wt) water, more preferably greater than 50% (by wt) water, and most preferably greater than 80% (by wt) water. Alcohols, such as ethyl alcohol and isopropyl alcohol, may be used at low concentrations (about 0.5% by weight of the formulation) to enhance hair penetration and/or reduce odor.

vii. Viscosity Modifying Agents

The formulations may contain one or more viscosity modifying agents, such as viscosity increasing agents. Classes of such agents include, but are not limited to, viscous liquids, such as polyethylene glycol, semisynthetic polymers, such as semisynthetic cellulose derivatives, synthetic polymers, such as carbomers, poloxamers, and polyethyleneimines (e.g., PEI-10), naturally occurring polymers, such as acacia, tragacanth, alginates (e.g., sodium alginate), carrageenan, vegetable gums, such as xanthan gum, petroleum jelly, waxes, particulate associate colloids, such as bentonite, colloidal silicon dioxide, and microcrystalline cellulose, surfactants, such as PPG-2 hydroxyethyl coco/isostearamide, emulsifiers, such as disteareth-75 IPDI, and salts, such as sodium chloride, and combinations thereof

viii. Antioxidants

The formulation may contain one or more antioxidants. Examples include, but are not limited to, tocopheryls, BHT, ascorbic acid, camellia sinensis leaf extract, ascorbyl palmitate, magnesium ascorbyl phosphate, carotenoids, resveratrol, triethyl citrate, arbutin, kojic acid, tetrahexydecyl ascorbate, superoxide dismutase, zinc, sodium metabisulfite, lycopene, ubiquinone, and combinations thereof.

ix. Opacifying Agents

The formulation may contain one or more opacifying agents. Opacifying agents are added to the formulations to make it opaque. Suitable opacifying agents include, but are not limited to, glycol distearate and ethoxylated fatty alcohols.

c. Forms of the Formulation

i. Sprays

The formulation may be in the form of a spray. The spray typically includes the active agent and a cosmetically acceptable carrier. In some embodiments, the carrier is water or a water and alcohol mixture. The spray formulation optionally includes an antioxidant, sunscreen agent, vitamin, protein, peptide, plant extract, humectant, oil, emollient, lubricant, thickener, hair conditioning agent, polymer, and/or surfactant. Preferably, the spray formulation includes a preservative. In some embodiments, the formulation includes a fragrance. In some embodiments, the formulation includes a surfactant. In some embodiments, the formulation contains water, fragrance, a preservative, and an active agent. In some embodiments, the formulation contains water, fragrance, a preservative, and an active agent. In some embodiments, the formulation contains water, a preservative, fragrance, an active agent, and an anti-static agent. In some embodiments, the formulation contains water, a preservative, fragrance, an active agent, and a hair conditioning agent. In some embodiments, the formulation contains water, a preservative, fragrance, an active agent, and a surfactant.

The hair spray formulations may be dispensed from containers that include aerosol dispensers or pump spray dispensers. Such dispensers are known in the art and are commercially available from a variety of manufacturers.

Propellant

When the hair spray formulation is dispensed from a pressurized aerosol container, a propellant may be used to force the formulation out of the container. Suitable propellants include, but are not limited to, a liquefiable gas or a

halogenated propellant. Examples of suitable propellants include dimethyl ether and hydrocarbon propellants such as propane, n-butane, iso-butane, CFCs, and CFC-replacement propellants. The propellants may be used singly or admixed.

The amount of propellant may range from about 10% to about 60% by weight of the formulation. The propellant may be separated from the hair repair formulation as in a two compartment container. Other suitable aerosol dispensers are those characterized by the propellant being compressed air, which can be filled into the dispenser using a pump or equivalent device prior to use. Conventional non-aerosol pump spray dispensers, i.e., atomizers, may also be used to apply the formulation to the hair.

ii. Conditioners

The formulation may be in the form of a conditioner. The conditioner typically includes the active agent in a suitable carrier. Additionally, the conditioner may include cationic polymers derived from polysaccharides, for example cationic cellulose derivatives, cationic starch derivatives, cationic guar derivatives and cationic locust bean gum derivatives, synthetic cationic polymers, mixtures or combinations of these agents. The formulation may comprise other synthetic or natural polymers or polymers derived from biological preparation processes, which are functionalized, where appropriate, for example with cationic or neutral groups. These polymers may have a stabilizing or strengthening action on the formulation, and/or a conditioning action (deposition on the surface of the skin or the hair).

The active agent may be included in any suitable concentration. Typical concentrations of active agent in the conditioner range from small amounts such as approximately 0.01% (by wt), preferably at least 0.1% (by wt), to large amounts, such as up to 50% (by wt). Preferably the conditioner contains the active agent in a concentration ranging from 0.1% (by wt) to 5% (by wt), more preferably from 0.1% wt to 3% (by wt). While greater concentrations of active agent could be present in the conditioner, they are generally not needed to achieve the desired results.

iii. Shampoos

The hair repair formulation may be in the form of a shampoo. The shampoo typically includes the active agent in a suitable carrier. The active agent may be included in any suitable concentration. Typical concentrations of the active agent in the shampoo range from small amounts such as approximately 0.01% (by wt), preferably at least 0.1% (by wt), to large amounts, such as up to 50% (by wt). Preferably the shampoo contains the active agent in a concentration ranging from 0.1% (by wt) to 5% (by wt), more preferably from 0.1% (by wt) to 3% (wt). While greater concentrations of active agent could be present in the shampoo, they are generally not needed to achieve the desired results.

Additionally, the shampoo may include from about 0.5% to about 20% by weight of a surfactant material. Surfactants utilized in shampoo compositions are well-known in the art and are disclosed, for example, in U.S. Pat. No. 6,706,258 to Gallagher et al. and U.S. Pat. No. 7,598,213 to Geary et al.

iv. Creams, Lotions, Gels, and Polish

The hair, skin, or nail repair formulation may be in the form of a cream, lotion, gel, or polish. The cream, lotion, gel, or polish typically includes the active agent in a suitable carrier. The active agent may be included in any suitable concentration. Typical concentrations of the active agent in the cream, lotion, gel, or polish range from small amounts such as approximately 0.01% (by wt), preferably at least 0.1% (by wt), to large amounts, such as up to 50% (by wt). Preferably the cream or lotion contains the active agent in a concentration ranging from 0.1% (by wt) to 5% (by wt), more preferably from 0.1% (by wt) to 3% (by wt). While greater concentrations of active agent could be present in the cream or lotion, they are generally not needed to achieve the desired results.

Additionally, the formulation, depending on use, may include an oil, a hair conditioning agent, and/or a thickening agent. The cream, lotion, gel, or polish may also include a fragrance, a plant extract, and/or a surfactant. The cream, lotion, gel, or polish may be packaged in a tube, tub, bottle, or other suitable container.

v. Liquid Active Agent Formulations

In some embodiments, a liquid active agent formulation is provided, which is mixed at the time of use with a second formulation, such as a coloring or highlighting formulation. In these embodiments, the liquid active agent formulation may contain any suitable concentration of active agent in a suitable carrier, typically a diluent, such as described above. The concentration of the active agent is suitable to provide a mixture with the appropriate final volume and final concentration of active agent.

For example, a liquid active agent formulation can contain a concentration of active agent ranging from about 5% (by wt) to about 50% (by wt) or greater. In a preferred embodiment, the liquid active agent formulation contains about 20% (by wt) active agent.

For highlighting applications, prior to use, a sufficient volume of a liquid active agent formulation is mixed with a sufficient volume of a highlighting formulation to form a highlighting mixture having the desired concentration of active agent. Typical concentrations of the active agent in the highlighting mixture range from small amounts, such as approximately at least 0.01% (by wt), preferably at least 0.1% (by wt), to large amounts, such as up to 50% (by wt). Preferably the highlighting mixture contains the active agent in a concentration ranging from 0.1% (by wt) to 5% (by wt), more preferably from 0.1% (by wt) to 3% (wt). While greater concentrations of active agent could be present in the highlighting mixture, they are generally not needed to achieve the desired results.

III. Methods of Use

A. Treatment of Hair with Coloring Agents

a. Apply the Coloring Formulation to the Hair

The coloring formulation is generally applied to an individual's hair following normal hair coloring procedures that are known to those skilled in the art. Typically, hair color treatments include two complementary processes: applying a bleaching formulation to bleach the hair's natural pigment and/or other artificial pigments present in the hair, and diffusion of dye precursors into the hair, followed by coupling reactions that result in the formation of chromophores within the hair shaft, which are too large to diffuse out of the hair. The bleaching formulation typically contains a bleaching agent to lighten the hair and produce free thiol groups. The hair coloring formulation may be a highlighting formulation, such as formed by mixing bleach powder and developer. More complex colors may contain several precursors and many couplers, and may involve multiple reactions.

The dye precursors may contain several ingredients, each with different functions. The first ingredient is usually an alkalizing agent (usually ammonia and/or an ammonia substitute, such as monoethanolamine [MEA]). The alkalizing agent serves a number of roles in the hair colorant process including swelling the hair fiber to aid in diffusion of the dye precursors. The dye precursors generally include p-diamines and p-aminophenols. Precursors are oxidized to active inter-

mediates once they have penetrated the hair shaft. Intermediates then react with color couplers to create wash resistant dyes. More specifically, the intermediates, in the presence of an oxidant, couple with another oxidation dye intermediate molecule to form a large fused ring color compound within the hair shaft. The precursor intermediate should penetrate the hair shaft prior to the coupling reaction since the fused ring product is too large to penetrate the hair shaft. Couplers modify the color produced by the oxidation of precursor compounds. The primary difference between demi-permanent and permanent products is the alkalizing agent and the concentration of peroxide. The cuticle does not swell as greatly with demi-permanent dyes, making dye penetration less efficient compared to permanent coloring products.

Several coloring formulations use a reducing agent, such as sodium bisulfate, to break disulfide bonds in the hair, allowing deeper penetration of the hair coloring dyes into the hair. Specifically, the method includes reducing some of the disulfide linkages of the cystine in the hair shafts to thiol groups while breaking hydrogen bonds. The reducing process changes the chemical and cosmetic characteristics of the hair, which are undesirable.

The hair dyeing process may be followed by a shampoo and conditioning treatment, a neutralizing rinse or an acid balanced shampoo containing in addition to cationic or amphoteric surfactants, cation-active emollients and quarternary polymers. Alternately, the hair dying process may be followed by application of the active agent formulations described herein, before a shampoo and/or conditioning treatment.

b. Apply the Active Agent Formulation to the Hair

The active agent formulation may be applied simultaneously with the hair coloring formulation or subsequently to the application of the hair coloring formulation. For example, the active agent formulation may be mixed with the hair coloring treatment and the mixture, containing both the active agent and the hair coloring treatment, may be applied to the hair.

Alternatively, subsequent to coloring the hair, the active agent formulation, or a formulation thereof is applied to the hair. Although the active agent is typically applied on the same day as the coloring treatment, it may be applied later such as within 1 to 2 weeks following treatment with the reducing agent. Typically, the amount of active agent formulation (or a mixture of the active agent formulation and the hair coloring formulation) applied is sufficient to saturate the hair. The active agent may be applied to the hair as a single application, or application of the active agent may be repeated one or more times. Typically, the amount of active agent formulation applied in each application is sufficient to saturate the hair. The volume of active agent formulation applied to the hair in each application may be about 1 to about 100 mL per person depending on their length and volume of hair. In some embodiments, application of the active agent could be repeated immediately (e.g. within 10 to 15 seconds) or approximately 1, 5, 7.5, 10, 12.5, 15, 17.5, or 20 minutes after the first application.

The active agent can be rinsed and shampooed from the hair immediately following application, for example within 10, 15, 25, 30, 45, or 60 seconds, or two, three, four, or five minutes after application. Alternatively, the active agent may be rinsed from the hair within about 30 minutes following application, preferably between about 5 minutes and about 20 minutes, more preferably about 10 minutes after application of the active agent to the hair, depending on hair type.

If the active agent formulation is combined with the hair coloring treatment and applied as a mixture to the hair, then the mixture remains on the hair as long as needed for the hair coloring treatment. Typically the mixture is applied for approximately 10 minutes. The mixture is removed from the hair in accordance with standard methods for hair coloring treatments, e.g., rinse and shampoo, approximately 10 minutes after applying the mixture.

The active agent formulation is rinsed from the hair after its application. The hair may be rinsed and subsequently washed immediately (e.g. within 10 to 15 seconds following application) after the final application of the active agent. Preferably, the hair is rinsed and/or washed about 10 minutes or later after the final application of the active agent, such as about 15 minutes to about 30 minutes, optionally about 20 minutes after repeated application of the active agent to the hair.

The active agents are generally washed from the individual's hair on the same day as they are applied. In contrast, traditional perms which use only hydrogen peroxide (and do not involve the addition of the active agent) are generally not washed for at least 48 hours following application (washing the hair prior to 48 hours following a traditional permanent treatment may result in significant loss in the amount of curl in the hair and/or cause damage to the hair).

The formulation described herein improves hair quality, such as appearance (e.g., sheen) and feel, and decreases hair breakage when the hair is subjected to treatments, such as coloring or permanent waving.

In some embodiments, hair breakage decreases by 5, 10, 15, 20, 25, 30, 35, 40, 45, or 50% or higher after treatment with the active agent compared to untreated hair from the same individual. Hair breakage is a significant problem encountered during coloring and other treatments.

B. Chemical Treatment of Hair with a Reducing Agent

In one embodiment, prior to treatment with the active agent, the hair has been subjected to a reducing agent used for waving (also referred to herein as hair perming or permanent waves), and/or curling of the hair.

a. Apply a Reducing Agent to the Hair

The first step in waving or curling hair is breaking the cysteine disulfide bonds to form free thiol moieties. The process for breaking the cysteine disulfide bonds is via application of a reducing agent. The process for applying the reducing agent involves following normal perming or hair straightening procedures that are known to those skilled in the art. For example, to perm hair, the hair is first washed and set on perm rods of various sizes. Second, a reducing agent, such as thioglycolate reducing solution or lotion is applied to the hair. The hair is allowed to set for a specified period of time, and then the thioglycolate solution is rinsed from the hair.

The application of hydrogen peroxide in this process is optional. In some processes, such as when treating previously chemically treated hair, hydrogen peroxide is generally not used. In other processes, such as when perming virgin hair, hydrogen peroxide may be added. In these embodiments, hydrogen peroxide is typically added after the reducing agent is rinsed out. Then the hydrogen peroxide is rinsed from the hair prior to adding the active agent.

b. Apply the Active Agent

Subsequent to the reducing treatment, one or more of the active agent, or a formulation thereof is applied to the hair. Although the agent is typically applied on the same day as treatment with the reducing agent, it may be applied later such as within 1 to 2 weeks following treatment with the reducing agent.

Typically, the amount of active agent formulation applied is sufficient to saturate the hair. The agent is generally rinsed

and shampooed from the hair after the desired level of hair waving or curling is achieved. In some embodiments, the active agent is rinsed from the hair immediately (e.g. within 10, 15, 25, 30, 45, or 60 seconds following application) following the final application of the active agent. Alternatively the hair may be rinsed and washed about within about 30 minutes following application, preferably between about 5 minutes and about 20 minutes, more preferably about 10 minutes after the final application of the active agent to the hair, depending on the hair type. The active agent can be rinsed from the hair within 10, 15, 25, 30, 45, 60 seconds from the hair after application, and still achieve a desired level of hair waving or curling.

The active agent may be applied to the hair as a single application, or application of the agent may be repeated one or more times. Typically, the amount of active agent formulation applied in each application is sufficient to saturate the hair. In some embodiments, the volume of active agent formulation applied to the hair in each application is about 1 to about 10 mL per perm rod. In some embodiments, application of the active agent could be repeated immediately (e.g. within 10 to 15 seconds) or approximately 1, 5, 7.5, 10, 12.5, 15, 17.5, or 20 minutes after the first application. In some embodiments, the second application is about 7 minutes to about 10 minutes after the first application.

The active agent is rinsed from the hair after its application. The hair may be rinsed and washed immediately (e.g. within 10 to 15 seconds following application) after final application of the active agent. Alternatively the hair may be rinsed and washed about 10 minutes or later after the final application of the active agent, such as about 15 minutes to about 30 minutes, preferably about 20 minutes after repeated application of the active agent to the hair.

The active agents are generally washed from the individual's hair on the same day as they are applied. In contrast, traditional perms which use only hydrogen peroxide (and do not involve the addition of the active agent) are generally not washed for at least 48 hours following application (washing the hair prior to 48 hours following a traditional permanent treatment may result in significant loss in the amount of curl in the hair and/or cause damage to the hair).

The formulations described herein can be applied to hair to improve hair quality, such as appearance (e.g., sheen) and feel, and decrease hair breakage when the hair is subjected to subsequent treatments, such as coloring.

In some embodiments, hair breakage decreases by 5, 10, 15, 20, 25, 30, 35, 40, 45, or 50% or higher after application of the active agent compared to untreated hair from the same individual. Hair breakage is a significant problem encountered during coloring and other treatments.

C. Treatment of Skin or Nails with the Active Agent

In one embodiment, a formulation containing one or more of the active agents is applied to the skin or nails. Application of the active agent formulation to skin or nails can help repair damaged disulfide bonds due to natural wear and tear or natural aging.

In some embodiments the active agent formulation is in the form of a cream or lotion, which is suitable for application to the skin or nails. In other embodiments, the active agent formulation is in the form of a gel or polish, which is suitable for application to the nails. Typically, the amount of active agent formulation applied is sufficient to treat the damaged keratin in the skin or nails. The active agent formulation may be applied to the skin or nails in a single application, or application of the formulation may be repeated one or more times, as needed, to achieve the desired effect of repairing keratin damage and/or strengthening the skin or nails.

IV. Kit

Kits for treating hair are provided. In one embodiment, the kit typically contains a first formulation for coloring hair. The hair coloring formulations typically include a reducing agent capable of reducing disulfide bonds in hair to produce free thiol groups. The kit also includes a second formulation containing an effective amount of the active agent.

The kit may further include a developer bottle, gloves, shampoo, conditioner, and/or an odor eliminator. Instructions for use of the kit are also typically provided.

Typically the kit contains more than one container (or more than one compartment in a given container) to ensure that the lightening agent (e.g., peroxides) or the coloring agent is stored separately from the active agent.

A. First Formulation

The first formulation in the kit can be a coloring treatment. The first formulation may be formulated as two or more components which may be mixed together before application to the hair. For example, the first formulation may be in the form of two components such as a dye precursor and an oxidant. Typically, the hair coloring formulation contains a reducing agent capable of reducing the disulfide bonds in hair and producing reduced free thiol groups. Suitable reducing agents include, but are not limited to, thioglycolic acid, thiolactic acid, dihydrolipoate, thioglycerol, mercaptopropionic acid, sodium bisulfite, ammonium bisulfide, zinc formaldehyde sulfoxylate, sodium formaldehyde sulfoxylate, sodium metabisulfite, potassium borohydride, pegylated thiols and hydroquinone. The amount of the reducing agent in the first formulation is sufficient to rupture a sufficient number of disulfide bonds for effective diffusion of the hair coloring ingredients as would be appreciated by one of skill in the art.

The components of the first formulation may differ depending on the hair coloring treatment desired (such as for semi-permanent, demi-permanent, or permanent hair color), the texture of the hair, the sensitivity of the user's skin, and such the like. Hair coloring formulations for different hair coloring treatment, hair texture, and hair sensitivity are known to those of skill in the art.

B. Active Agent Formulation

The second formulation contains one or more active agents in an effective amount. Suitable formulations containing the active agents are discussed above. The second formulation may be in any suitable form. Suitable forms include, but are not limited to, low to moderate viscosity liquids, lotions, milks, mousses, sprays, gels, creams, shampoos, conditioners, and the like. The second formulation will be present in a suitable container, which depends on the form of the formulation.

In one embodiment, the active agent formulation is provided as two or more separate ingredients. For example, the active agent may be provided as a dry powder in a sealed package and the excipient provided in a vial or other container. A suitable mixing container for the active agent and the excipient may be provided.

In some embodiments, the active agent formulation (or second formulation) is mixed with the first formulation (or hair coloring treatment), and the mixture is applied to the hair.

C. Other Materials in the Kit

The kit optionally contains shampoos and conditioners. Suitable shampoos and conditioners include, but are not limited to LiQWd® Hydrating Shampoo and LiQWd® Hydrating Conditioner.

The kit may further contain an odor eliminator. The odor eliminator can be incorporated into the first or second formulation, or a mixture thereof. Alternately, the odor eliminator is present in a suitable container for use before or after washing the second formulation from the hair. Some suitable odor eliminators are known to those of ordinary skill in the art.

It is understood that the disclosed method and formulations are not limited to the particular methodology, protocols, and reagents described as these may vary. It is also to be understood that the terminology used herein is for the purpose of describing particular embodiments only, and is not intended to limit the scope of the present invention which will be limited only by the appended claims.

EXAMPLES

Example 1

Color Retention and Texture of Colored Hair Treated with the Active Agent Formulation

General

Three hair samples were obtained from a human subject and cut in i/2 inch wide wefts.

Coloring Formulation:

The permanent hair coloring formulation was obtained from a L'Oreal® permanent hair coloring service (L'Oreal® Majirel permanent color #10 with 20 volume peroxide).

Active Agent Formulation:

Maleic acid, at a concentration of 200 mg in 10 g total solution (water) was used.

Methods

The hair samples were washed with a clarifying shampoo then towel dried. The samples were then colored with the L'Oreal® permanent hair color service, which was left on the hair samples for approximately 35-40 minutes.

The first color treated hair sample ("control") was subsequently rinsed and washed with Liqwd® Hydrating Shampoo and Conditioner five times before being photographed.

The active agent formulation was applied to the second and third color treated hair samples via a spray bottle and massaging using the fingers. The active agent formulation was left on the second hair sample for a period of about 1 minute and on the third sample for a period of about 10 minutes. The hair samples were subsequently rinsed, and then washed with Liqwd® Hydrating Shampoo and Conditioner five times before being examined.

Results:

The hair samples treated with the active agent formulation showed better color retention, more shine, and less frizz than the control. The hair samples treated with the active agent formulation felt smoother to the touch and combined with the lower frizz and added sheen gave an overall healthier appearance over the control.

Example 2

Comparison of Color Retention in Traditionally Permed Hair and Hair Permed Using the Active Agent Formulations

Method

A ½ inch wide weft of hair sample, obtained from a human subject, was washed with clarifying shampoo then towel dried. Ammonium thioglycolate or dithiothreitol was mechanically pulled through the hair with a wide and a fine toothcomb several times then left on the hair for 10 minutes to 1 hour. The hair was then rinsed for 30 seconds to 1 minute with water, and then towel dried.

The active agent formulation, described in Example 1 (Maleic acid in water), was then applied via a needle nose applicator drenching the hair and leaving it on for 7.5 minutes. This step was repeated, for a total of 15 minutes. The hair was then rinsed for 1-2 minutes, shampooed, and then conditioned with various salon shampoo and conditioner brands, including LiQWd® Hydrating Shampoo and Hydrating Conditioner.

A second sample of hair was straightened, as described above, but using hydrogen peroxide instead of the active agent formulation. The hair samples were washed and conditioned repeatedly.

Comparison of Hair Color:

After both hair samples were washed five times using LiQWd® Hydrating Shampoo and LiQWd® Hydrating Conditioner, the samples were examined for their color retention.

Results

The hair sample treated with the active agent formulation displayed a color closer in intensity to the hair sample prior to the first washing, compared to the hair treated with hydrogen peroxide.

Example 3

Comparison of Hair Treated with Highlighting Formulation Applied Simultaneously with Active Agent Formulation and Hair Treated with Highlighting Formulation Alone

The active agent formulation in Example 1 contained maleic acid at concentrations of 2.0 g in 10 g total solution (water).

Two swatches of human hair were tested. A sample was taken from the same head, 1 inch wide, and split in half. The color was medium brown and had been previously color treated with an unknown professional hair color.

Swatch 1, ½ inch wide and 8 inches long, was lightened with traditional highlighting ingredients mixed with the active agent formulation. 1 oz of Joico Verocolor Veroxide developer-20 volume was mixed with 1 oz Joico Verolight powder bleach to form the highlighting formulation. Then 9 mL of the active agent formulation was added to the highlighting formulation to form a mixture.

The mixture was applied on the Swatch 1 hair with an applicator brush as the hair lay on aluminum foil. The foil was then wrapped around the swatch and allowed to process for 35 minutes. The swatch was rinsed and shampooed one time.

Swatch 2, the control, ½ inch wide and 8 inches long, was lightened with traditional highlighting ingredients in the absence of the active agent formulation. 1 oz of Joico Verocolor Veroxide developer-20 volume was mixed with 1 oz Joico Verolight powder bleach to form a highlighting formulation with a creamy consistency.

The highlighting formulation was applied on the Swatch 2 hair with an applicator brush as the hair lay on aluminum foil. The foil was then wrapped around the swatch and allowed to process for 35 minutes. The swatch was rinsed and shampooed one time.

Results

A noticeable difference in hair quality between Swatch 1 and Swatch 2 was observed. Swatch 1 hair was softer, less frizzy, appeared hydrated, with more shine than the control, Swatch 2.

Both swatches were washed and conditioned 5 more times with the same noticeable benefits of Swatch 1 (treated with the mixture of highlighting formulation and active agent

formulation) compared to the control, Swatch 2 (treated with highlighting formulation, alone).

Example 4

Comparison of Hair Treated with Bleaching Formulation Applied Simultaneously with Active Agent Formulation and Hair Treated with Bleaching Formulation Alone

General

Two hair samples were obtained from a human subject and cut in ½ inch wide wefts.

Methods

(1) 0.5 ounces of powder lightener (Clairol Professional, Basic White) and 0.5 ounces of conditioning cream developer (Redken, Blonde Icing) were combined to form a bleaching mixture. 3.5 g of 2-(methacryloyloxy)ethan-1-aminium (Z)-3-carboxyacrylate (12 wt % in water) was added to the bleaching mixture and thoroughly mixed with a brush.

(2) The bleaching mixture prepared was brushed onto the swatches of hair with a brush in order to thoroughly coat the strands of hair. The mixture coated hair was wrapped in aluminum paper and allowed to stand under ambient conditions for a period of two hours.

(3) After the two hour bleaching period the swatches of hair were washed with shampoo and the hair was subsequently allowed to air dry.

Results

A noticeable difference in hair quality between Swatch 1 and Swatch 2 was observed. Swatch 1 hair was demonstrated no discernible breakage, great feel, and a healthy appearance while the control (treated with bleaching formulation, alone) showed some breakage, had a rough feel, and was frayed with an unhealthy appearance.

Example 5

Comparison of Hair Treated with Bleaching Formulation Applied Simultaneously with Active Agent Formulation and Hair Treated with Bleaching Formulation Alone

General

Two hair samples were obtained from a human subject and cut in ½ inch wide wefts.

Methods

(1) 0.5 ounces of powder lightener (Clairol Professional, Basic White) and 0.5 ounces of conditioning cream developer (Redken, Blonde Icing) were combined to form a bleaching mixture. 3.5 g of prop-2-en-1-aminium (Z)-3-carboxyacrylate (10 wt % in water) was added to the bleaching mixture and thoroughly mixed with a brush.

(2) The bleaching mixture prepared was brushed onto the swatches of hair with a brush in order to thoroughly coat the strands of hair. The mixture coated hair was wrapped in aluminum paper and allowed to stand under ambient conditions for a period of two hours.

(3) After the two hour bleaching period the swatches of hair were washed with shampoo and the hair was subsequently allowed to air dry.

Results

A noticeable difference in hair quality between Swatch 1 and Swatch 2 was observed. Swatch 1 hair was demonstrated no discernible breakage, great feel, and a healthy appearance while the control (treated with bleaching formulation, alone) showed some breakage, had a rough feel, and was frayed with an unhealthy appearance.

Example 6

Comparison of Traditional Perm Versus Perm Using Maleic Acid

General

Hair samples were obtained from a human subject and cut in ½ inch wide wefts.

Reducing Agents:

Ammonium thioglycolate (ATG) was obtained from a permanent wave kit manufactured by Zotos. 300 mg of Dithiothreitol in a 10 g solution was also used as the reducing agent.

Active Agent Formulation:

Maleic acid at a concentration of 200 mg in 10 g total solution (water) was used.

Methods

Method for Perming Hair Using the Active Agent

The hair was washed with clarifying shampoo, towel dried, and then rolled around a perm rod. Ammonium thioglycolate or dithiothreitol was then applied to the hair and left on the hair for 10 minutes to 1 hour. The hair was then rinsed for 30 seconds to 1 minute and then blotted dry with a towel.

The active agent formulation was applied to the hair, via a needle nose applicator, drenching the hair. The active agent formulation was left on the hair for a period of about 7.5 minutes. The hair was drenched for a second time with the active agent formulation and left for a second 7.5 minutes, for a total of 15 minutes. The hair was then rinsed with water for about 1-2 minutes then unrolled from the perm rods. After the hair was removed from the perm rods, the hair was shampooed and conditioned with various salon shampoo and conditioner brands, including LiQWd® Hydrating Shampoo and Hydrating Conditioner. The washing and drying steps were repeated 40 times.

A second portion of hair was permed as described above, except, hydrogen peroxide was used instead of the active agent formulation.

Results

Both perms (utilizing the active agent formulation or hydrogen peroxide) showed only slight reduction in the overall curl after 40 cycles of washing and drying with the same shampoo and conditioner. However, the appearance and texture of the perm using the active agent formulation showed more sheen and less frizz compared to the perm using hydrogen peroxide.

Example 7

Comparison of Hair Breakage Due to Repeated Application of Traditional Perm and the Active Agent Formulation

Methods

Two hair samples were obtained. Both samples were treated with dithiothreitol or ammonium thioglycolate as described in Example 6. One of the hair samples was subsequently treated with the active agent formulation (Maleic acid in water), while the other was neutralized with hydrogen peroxide. The process was completed the same day for the hair treated with the active agent formulation. The process was completed in three days with hydrogen peroxide (traditional perm).

The procedure was repeated three times for each hair sample over a 48 hour time period.

Results

Upon visual inspections, the second hair sample treated with the active agent formulation showed little or no signs of breakage. However, the first hair sample treated with hydrogen peroxide showed significant breakage.

Example 8

Comparison of the Extent of Damage to Hair Previously Relaxed with a Japanese Relaxer

Methods

Two samples of hair, the first previously straightened with a Japanese relaxer (Yuko), and the second previously straightened with a no lye relaxer (African Pride Miracle Deep Conditioning) were obtained. The samples were treated as described in Examples 6 and 7 using the active agent formulation (Maleic acid in water).

Another hair sample, previously straightened with a no lye relaxer (African Pride Miracle Deep Conditioning) was obtained. The sample was treated with a traditional hair straightening perm (Zotos).

Results

The hair samples treated with the active agent formulation showed no noticeable damage. However, the sample treated with a traditional perm showed significant breaking, even during application.

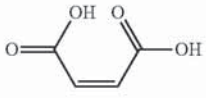
Unless defined otherwise, all technical and scientific terms used herein have the same meanings as commonly understood by one of skill in the art to which the disclosed invention belongs. Publications cited herein and the materials for which they are cited are specifically incorporated by reference.

Those skilled in the art will recognize, or be able to ascertain using no more than routine experimentation, many equivalents to the specific embodiments of the invention described herein. Such equivalents are intended to be encompassed by the following claims.

We claim:

1. A method for bleaching hair comprising:

(a) mixing a formulation comprising an active agent with a bleaching formulation, wherein the active agent has the formula:



or salts thereof;

and

(b) applying the mixture to the hair;

wherein the active agent in the mixture is at a concentration ranging from about 0.1% by weight to about 50% by weight; and

wherein the mixture does not contain a hair coloring agent.

2. The method of claim **1**, wherein the formulation comprising the active agent further comprises one or more pharmaceutically acceptable excipients selected from the group consisting of water, surfactants, vitamins, natural extracts, preservatives, chelating agents, perfumes, preservatives, antioxidants, proteins, amino acids, humectants, fragrances, emollients, penetrants, thickeners, viscosity modifiers, hair fixatives, film formers, emulsifiers, opacifying agents, propellants, liquid vehicles, carriers, salts, pH adjusting agents, neutralizing agents, buffers, hair conditioning agents, anti-static agents, anti-frizz agents, anti-dandruff agents, and combinations thereof.

3. The method of claim **2**, wherein the one or more excipients are present in an amount ranging from about 50 wt % to about 90 wt % of the formulation.

4. The method of claim **1**, wherein the active agent is present in an amount ranging from about 1 wt % to about 10 wt % of the formulation.

5. The method of claim **1**, wherein the active agent is present in an amount ranging from about 0.5 to 3 wt % of the formulation.

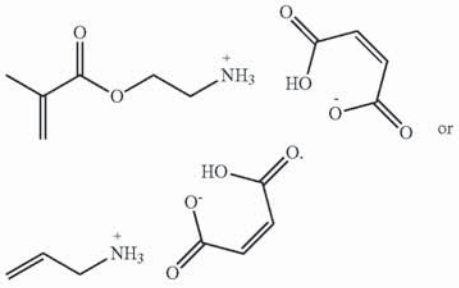
6. The method of claim **1**, wherein the formulation comprising the active agent is in the form of a liquid, a gel, a cream, or a lotion.

7. The method of claim **1**, wherein step (b) is repeated one or more times.

8. The method of claim **1**, further comprising:

(c) rinsing, shampooing, or conditioning the hair, or a combination thereof, wherein step (c) occurs subsequent to step (b).

9. The method of claim **1**, wherein the active agent is:



10. The method of claim **1**, wherein the mixing occurs at the time of use and prior to application of the mixture to the hair.

* * * * *

EXHIBIT B

US009668954B2

(12) **United States Patent**
Pressly et al.

(10) **Patent No.: US 9,668,954 B2**
(45) **Date of Patent: *Jun. 6, 2017**

(54) **KERATIN TREATMENT FORMULATIONS AND METHODS**

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(*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 0 days.

This patent is subject to a terminal disclaimer.

(21) Appl. No.: **15/415,464**

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(63) Continuation of application No. 15/290,593, filed on Oct. 11, 2016, which is a continuation of application No. 15/087,415, filed on Mar. 31, 2016, now Pat. No. 9,498,419, which is a continuation of application No. 14/713,885, filed on May 15, 2015, now Pat. No. 9,326,926.

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(51) **Int. Cl.**

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A61Q 5/08	(2006.01)
A61Q 5/12	(2006.01)
A61K 8/41	(2006.01)
A61K 8/42	(2006.01)
A61K 8/06	(2006.01)
A61K 8/34	(2006.01)
A61K 8/84	(2006.01)

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(58) **Field of Classification Search**

None

See application file for complete search history.

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(57) **ABSTRACT**

Formulations, kits, and methods for rebuilding the disulfide bonds in keratin found in hair, skin, or nails. Hair that is damaged due to a hair coloring treatment and/or other reducing treatment, such as during a permanent wave, can be treated with the formulations containing one or more active agents. The formulations may be applied subsequent to a hair coloring treatment or simultaneously with a hair coloring treatment. Use of the active agent formulations during a permanent wave treatment prevents the reversion of the hair to its previous state, for at least one week, preferably at least three months, more preferably at least one year, most preferably greater than one year, after one or more than one application of the formulation. Application of the active agent formulation to skin or nails can help repair damaged disulfide bonds due to natural wear and tear or natural aging.

30 Claims, No Drawings

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KERATIN TREATMENT FORMULATIONS AND METHODS

CROSS-REFERENCE TO RELATED APPLICATIONS

This application is a continuation of U.S. application Ser. No. 15/290,593, filed Oct. 11, 2016, which is a continuation of U.S. application Ser. No. 15/087,415, filed Mar. 31, 2016, now U.S. Pat. No. 9,498,419, which is a continuation of U.S. application Ser. No. 14/713,885, filed May 15, 2015, now U.S. Pat. No. 9,326,926, which claims benefit and priority to U.S. Provisional Application Ser. No. 61/994,709, filed May 16, 2014, the disclosures of which are incorporated herein by reference in their entirety.

FIELD OF THE INVENTION

The present invention generally relates to formulations and methods for treating keratin in hair, skin, or nails, and in particular for strengthening and/or repairing hair during or after a coloring or permanent wave treatment.

BACKGROUND OF THE INVENTION

Hair coloring is currently a globally accepted fashion phenomenon. Color treatments include hair coloring, highlighting, and bleaching. The coloring products can be categorized in several types, which include permanent, demi-permanent, semi-permanent, and temporary coloring formulations. Permanent hair coloring products make up the majority of the market worldwide.

Significant effort has been directed towards developing various approaches to hair dyeing; these include, oxidative dyes, direct action dyes, natural dyes, metallic dyes and reactive dyes. Many hair coloring formulations, in particular permanent coloring formulations, use reducing agents to break the disulfide bonds in the hair allowing deeper penetration of the hair coloring dyes and bleaching agents into the hair.

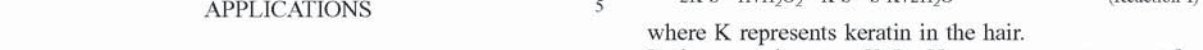
Disulfide bond linkages in hair are also broken by application of reducing agents, such as during permanent wave and hair straightening process. After the disulfide bonds are broken, the hair is placed in stress to establish the final style (e.g., straight, wavy, or curly), and the disulfide bonds are re-established.

Thioglycolic acid, particularly as the ammonium salt, is often used to cleave the cysteine disulfide bonds present in hair. Sodium bisulfite is another example of a known reducing agent commonly used in various dyes and bleaching agents in color treatments.

Typically, oxidation to restore the reduced bond is partially obtained when an oxidizing agent, such as hydrogen peroxide is present in a coloring formulation and/or by exposing the hair to atmospheric oxygen. However, this oxidation step can be very slow and can leave the hair frizzy and damaged.

Similarly, hair undergoing a permanent wave treatment is typically treated with a reducing agent followed by an oxidizing agent. Hydrogen peroxide is optionally added in a second step to restore the hair to its prior state. The newly formed disulfide bonds of the treated hair are under stress to maintain the hair's new shape; thus, they break easily resulting in a reversion of the hair style over time.

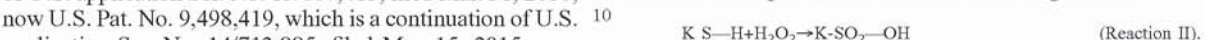
The use of peroxides in the hair styling process can result in damaged hair, removal of non-natural color from the hair, and/or leave the hair frizzy. Furthermore, some latent reduced thiols may remain in the hair even after oxidative treatment. Hair styling treatments with peroxides involve the following reaction with thiol groups:



$$2K\text{-}S\text{—}H+H_2O_2 \rightarrow K\text{-}S\text{—}S\text{-}K+2H_2O \quad \text{(Reaction I)}$$

where K represents keratin in the hair.

In the case where two K-S—H groups are not present for Reaction I to take place, it is believed that the following reaction takes place, which results in damaged hair:



$$K\ S\text{—}H+H_2O_2 \rightarrow K\text{-}SO_2\text{—}OH \quad \text{(Reaction II).}$$

In addition to being a major component in hair, keratin is also a major component in skin and nails. There are a number of different types of keratin and they are generally grouped as soft or hard keratins. Soft keratins are more prevalent in skin, while hard keratins predominate in hair and nails. Nails, in particular, are made of a modified keratin similar to that found hair. The disulfide bonds of the keratin in nails contribute to their impermeability. Therefore, damage to the disulfide bridges of keratin present in skin or nails can result in unhealthy and/or flaky skin or nails. Maintaining the disulfide bridges of keratin therefore helps to keep skin healthy and prevents cracking and splitting in nails.

Substantial improvement is needed in the areas of color saturation, color development, precise initial color consistency, improved wash fastness, and improved hair conditioning when applying color treatments. For example, the attainment of precise initial colors that are retained by the hair for a desirable time period has remained an elusive goal. The coloring formulations also cause severe hair damage, especially when coloring treatments are repeated. Moreover, various standard daily actions to the hair, for example hair brushing, hair blow-drying, and sun light exposure can cause even more damage to the hair.

Similar damage to the hair can also result from permanent wave treatments. In both coloring and permanent wave processes, improvements are also needed to repair damage and/or to strengthen the hair during or after such styling treatments. Additionally, improved treatments and methods are needed which can be applied to skin and nails to repair damaged keratin.

There is a need for hair formulations and treatments that repair and/or strengthen keratin in hair damaged from coloring and/or permanent wave treatments using reducing treatments.

There is also a need for hair formulations and treatments that can repair latent reduced thiols present in hair.

There is also a need for formulations and treatments that can repair damage to keratin present in skin and hair.

Therefore, it is an object of this invention to provide improved formulations and methods for repairing and/or strengthening damaged hair.

It is also an object of this invention to provide methods for using formulations that repair and/or strengthen hair after and/or during coloring or permanent wave treatments.

It is also an object of this invention to provide formulations and methods for using these formulations to repair and/or strengthen hair after a reducing treatment.

It is also an object of this invention to provide formulations and methods for using these formulations that repair and/or strengthen keratin in hair, skin or nails due to natural wear and tear or due to natural aging.

SUMMARY OF THE INVENTION

Formulations, kits, and methods for restoring hair that has been broken during a hair coloring or permanent wave

treatment are disclosed. The formulations have similar benefits when used with different color chemical processes, such as bleaching, highlights, lowlights, semi-permanent, demi-permanent, and permanent color. Improved methods of styling hair, for example permanent hair waving and hair curling are also provided. The formulations can be applied each time the hair is washed or daily, once-weekly, twice-weekly, biweekly, once-monthly, every other month, or at less frequent intervals. Preferably, the formulations are applied once-monthly to achieve the desired results.

Traditional methods of permanent hair waving, hair curling, or straightening use hydrogen peroxide after a reducing treatment. The process generally takes about three days to complete. The methods disclosed herein use active agents to repair the hair; these active agents are washed from the individual's hair on the same day that they are applied to the hair. Under the same conditions, such as temperature and moisture, hair treated with the formulations disclosed herein takes a longer time to revert to its prior state as compared to the same hair that is treated with hydrogen peroxide.

The formulations disclosed herein contain one or more polyfunctional compounds. The polyfunctional compound contains at least one ionizable functional group capable of forming ionic bonds, and the polyfunctional compound also contains at least one functional group capable of forming a covalent bond with a thiol group. In some embodiments, the polyfunctional compounds contain at least two ionizable groups. Optionally, the formulation is applied at the same time as the hair coloring or permanent wave treatment. Alternatively, the formulation may be applied after the hair coloring or permanent wave treatment or to damaged hair. For example, the formulations can be applied within one week of the hair being treated and/or damaged, preferably within three days, more preferably within two days, most preferably immediately after application of the coloring or permanent wave treatment.

DETAILED DESCRIPTION OF THE INVENTION

I. Definitions

The term "hair" refers to one or more than one strand of hair, as well as the natural components of hair, such as oil from a body. Hair also refers to virgin hair or processed hair, for example hair that has been exposed to hair waving or hair straightening formulations.

"Pharmaceutically acceptable" and "cosmetically acceptable" are used interchangeably and refer to those compounds, materials, and/or formulations, which are, within the scope of sound medical judgment, suitable for use in contact with the tissues of human beings and animals without excessive toxicity, irritation, allergic response, or other problems or complications commensurate with a reasonable benefit/risk ratio. More specifically, pharmaceutically acceptable refers to a material, compound, or formulation that is suitable for use in contact with the skin, scalp, or hair. Pharmaceutically acceptable materials are known to those of ordinary skill in the art.

"Shampoo", as used herein, generally refers to a liquid or semi-solid formulation applied to hair that contains detergent or soap for washing the hair.

"Conditioner", as used herein, generally refers to a formulation (e.g., liquid, cream, lotion, gel, semi-solid) applied to hair to soften the hair, smooth the hair, and/or change the sheen of the hair.

"Analog" and "derivative" are used herein interchangeably, and refer to a compound that possesses the same core as the parent compound, but differs from the parent compound in bond order, the absence or presence of one or more atoms and/or groups of atoms, or a combination thereof. The derivative can differ from the parent compound, for example, in one or more substituents present on the core, which may include one or more atoms, functional groups, or substructures. In general, a derivative can be formed, at least theoretically, from the parent compound via chemical and/or physical processes.

"Electrophilic group" or "electrophilic moiety" are used interchangeably and refer to one or more functional groups or moieties that have an affinity for or attract electrons.

"Nucleophilic group" or "nucleophilic moiety" are used interchangeably and refer to one or more functional groups or moieties that are electron rich and are capable of reacting with electrophilic groups.

"Michael acceptor", as used herein, is a species of electrophilic groups or moieties that participates in nucleophilic addition reactions. The Michael acceptor can be or can contain an α,β-unsaturated carbonyl-containing group or moiety, such as a ketone. Other Michael acceptors include pi-bonds, such as double or triple bonds conjugated to other pi-bond containing electron withdrawing groups, such as nitro groups, nitrile groups, and carboxylic acid groups.

"Carboxylic acid," as used in here refers to the group —COOH. Unless specified otherwise the term carboxylic acid embraces both the free acid and carboxylate salt.

"Alkyl", as used herein, refers to the radical of saturated or unsaturated aliphatic groups, including straight-chain alkyl, alkenyl, or alkynyl groups, branched-chain alkyl, alkenyl, or alkynyl groups, cycloalkyl, cycloalkenyl, or cycloalkynyl (alicyclic) groups, alkyl substituted cycloalkyl, cycloalkenyl, or cycloalkynyl groups, and cycloalkyl substituted alkyl, alkenyl, or alkynyl groups. Unless otherwise indicated, a straight chain or branched chain alkyl has 30 or fewer carbon atoms in its backbone (e.g., C_1-C_{30} for straight chain, C_3-C_{30} for branched chain), more preferably 20 or fewer carbon atoms, more preferably 12 or fewer carbon atoms, and most preferably 8 or fewer carbon atoms. In some embodiments, the chain has 1-6 carbons. Likewise, preferred cycloalkyls have from 3-10 carbon atoms in their ring structure, and more preferably have 5, 6 or 7 carbons in the ring structure. The ranges provided above are inclusive of all values between the minimum value and the maximum value.

The term "alkyl" includes both "unsubstituted alkyls" and "substituted alkyls", the latter of which refers to alkyl moieties having one or more substituents replacing a hydrogen on one or more carbons of the hydrocarbon backbone. Such substituents include, but are not limited to, halogen, hydroxyl, carbonyl (such as a carboxyl, alkoxycarbonyl, formyl, or an acyl), thiocarbonyl (such as a thioester, a thioacetate, or a thioformate), alkoxyl, phosphoryl, phosphate, phosphonate, a phosphinate, amino, amido, amidine, imine, cyano, nitro, azido, sulfhydryl, alkylthio, sulfate, sulfonate, sulfamoyl, sulfonamido, sulfonyl, heterocyclyl, aralkyl, or an aromatic or heteroaromatic moiety.

Unless the number of carbons is otherwise specified, "lower alkyl" as used herein means an alkyl group, as defined above, but having from one to ten carbons, more preferably from one to six carbon atoms, in its backbone structure. Likewise, "lower alkenyl" and "lower alkynyl" have similar chain lengths. Preferred alkyl groups are lower alkyls.

The alkyl groups may also contain one or more heteroatoms within the carbon backbone. Examples include oxygen,

nitrogen, sulfur, and combinations thereof. In certain embodiments, the alkyl group contains between one and four heteroatoms.

"Alkenyl" and "Alkynyl", as used herein, refer to unsaturated aliphatic groups containing one or more double or triple bonds analogous in length (e.g., C_2-C_{30}) and possible substitution to the alkyl groups described above.

"Aryl", as used herein, refers to 5-, 6- and 7-membered aromatic rings. The ring may be a carbocyclic, heterocyclic, fused carbocyclic, fused heterocyclic, bicarbocyclic, or biheterocyclic ring system, optionally substituted as described above for alkyl. Broadly defined, "Ar", as used herein, includes 5-, 6- and 7-membered single-ring aromatic groups that may include from zero to four heteroatoms. Examples include, but are not limited to, benzene, pyrrole, furan, thiophene, imidazole, oxazole, thiazole, triazole, pyrazole, pyridine, pyrazine, pyridazine and pyrimidine. Those aryl groups having heteroatoms in the ring structure may also be referred to as "heteroaryl", "aryl heterocycles", or "heteroaromatics". The aromatic ring can be substituted at one or more ring positions with such substituents as described above, for example, halogen, azide, alkyl, aralkyl, alkenyl, alkynyl, cycloalkyl, hydroxyl, alkoxyl, amino, nitro, sulfhydryl, imino, amido, phosphonate, phosphinate, carbonyl, carboxyl, silyl, ether, alkylthio, sulfonyl, sulfonamido, ketone, aldehyde, ester, heterocyclyl, aromatic or heteroaromatic moieties, —CF_3, and —CN. The term "Ar" also includes polycyclic ring systems having two or more cyclic rings in which two or more carbons are common to two adjoining rings (the rings are "fused rings") wherein at least one of the rings is aromatic, e.g., the other cyclic rings can be cycloalkyls, cycloalkenyls, cycloalkynyls, aryls and/or heterocycles, or both rings are aromatic.

"Alkylaryl", as used herein, refers to an alkyl group substituted with an aryl group (e.g., an aromatic or hetero aromatic group).

"Heterocycle" or "heterocyclic", as used herein, refers to a cyclic radical attached via a ring carbon or nitrogen of a monocyclic or bicyclic ring containing 3-10 ring atoms, and preferably from 5-6 ring atoms, containing carbon and one to four heteroatoms each selected from non-peroxide oxygen, sulfur, and N(Y) wherein Y is absent or is H, O, (C_{1-4}) alkyl, phenyl or benzyl, and optionally containing one or more double or triple bonds, and optionally substituted with one or more substituents. The term "heterocycle" also encompasses substituted and unsubstituted heteroaryl rings. Examples of heterocyclic rings include, but are not limited to, benzimidazolyl, benzofuranyl, benzothiofuranyl, benzothiophenyl, benzoxazolyl, benzoxazolinyl, benzthiazolyl, benztriazolyl, benztetrazolyl, benzisoxazolyl, benzisothiazolyl, benzimidazolinyl, carbazolyl, 4aH-carbazolyl, carbolinyl, chromanyl, chromenyl, cinnolinyl, decahydroquinolinyl, 2H,6H-1,5,2-dithiazinyl, dihydrofuro[2,3-b] tetrahydrofuran, furanyl, furazanyl, imidazolidinyl, imidazolinyl, imidazolyl, 1H-indazolyl, indolenyl, indolinyl, indolizinyl, indolyl, 3H-indolyl, isatinoyl, isobenzofuranyl, isochromanyl, isoindazolyl, isoindolinyl, isoindolyl, isoquinolinyl, isothiazolyl, isoxazolyl, methylenedioxyphenyl, morpholinyl, naphthyridinyl, octahydroisoquinolinyl, oxadiazolyl, 1,2,3-oxadiazolyl, 1,2,4-oxadiazolyl, 1,2,5-oxadiazolyl, 1,3,4-oxadiazolyl, oxazolidinyl, oxazolyl, oxindolyl, pyrimidinyl, phenanthridinyl, phenanthrolinyl, phenazinyl, phenothiazinyl, phenoxathinyl, phenoxazinyl, phthalazinyl, piperazinyl, piperidinyl, piperidonyl, 4-piperidonyl, piperonyl, pteridinyl, purinyl, pyranyl, pyrazinyl, pyrazolidinyl, pyrazolinyl, pyrazolyl, pyridazinyl, pyridooxazole, pyridoimidazole, pyridothiazole, pyridinyl, pyridyl, pyrimidinyl, pyrrolidinyl, pyrrolinyl, 2H-pyrrolyl, pyrrolyl, quinazolinyl, quinolinyl, 4H-quinolizinyl, quinoxalinyl, quinuclidinyl, tetrahydrofuranyl, tetrahydroisoquinolinyl, tetrahydroquinolinyl, tetrazolyl, 6H-1,2,5-thiadiazinyl, 1,2,3-thiadiazolyl, 1,2,4-thiadiazolyl, 1,2,5-thiadiazolyl, 1,3,4-thiadiazolyl, thianthrenyl, thiazolyl, thienyl, thienothiazolyl, thienooxazolyl, thienoimidazolyl, thiophenyl and xanthenyl.

"Heteroaryl", as used herein, refers to a monocyclic aromatic ring containing five or six ring atoms containing carbon and 1, 2, 3, or 4 heteroatoms each selected from non-peroxide oxygen, sulfur, and N(Y) where Y is absent or is H, O, (C_1-C_8) alkyl, phenyl or benzyl. Non-limiting examples of heteroaryl groups include furyl, imidazolyl, triazolyl, triazinyl, oxazoyl, isoxazoyl, thiazolyl, isothiazoyl, pyrazolyl, pyrrolyl, pyrazinyl, tetrazolyl, pyridyl, (or its N-oxide), thienyl, pyrimidinyl (or its N-oxide), indolyl, isoquinolyl (or its N-oxide), quinolyl (or its N-oxide) and the like. The term "heteroaryl" can include radicals of an ortho-fused bicyclic heterocycle of about eight to ten ring atoms derived therefrom, particularly a benz-derivative or one derived by fusing a propylene, trimethylene, or tetramethylene diradical thereto. Examples of heteroaryl include, but are not limited to, furyl, imidazolyl, triazolyl, triazinyl, oxazoyl, isoxazoyl, thiazolyl, isothiazoyl, pyraxolyl, pyrrolyl, pyrazinyl, tetrazolyl, pyridyl (or its N-oxide), thientyl, pyrimidinyl (or its N-oxide), indolyl, isoquinolyl (or its N-oxide), quinolyl (or its N-oxide), and the like.

"Halogen", as used herein, refers to fluorine, chlorine, bromine, or iodine.

The term "substituted," as used herein, refers to all permissible substituents of the compounds described herein. In the broadest sense, the permissible substituents include acyclic and cyclic, branched and unbranched, carbocyclic and heterocyclic, aromatic and nonaromatic substituents of organic compounds. Illustrative substituents include, but are not limited to, halogens, hydroxyl groups, or any other organic groupings containing any number of carbon atoms, preferably 1-14 carbon atoms, and optionally include one or more heteroatoms such as oxygen, sulfur, or nitrogen grouping in linear, branched, or cyclic structural formats. Representative substituents include alkyl, substituted alkyl, alkenyl, substituted alkenyl, alkynyl, substituted alkynyl, phenyl, substituted phenyl, aryl, substituted aryl, heteroaryl, substituted heteroaryl, halo, hydroxyl, alkoxy, substituted alkoxy, phenoxy, substituted phenoxy, aroxy, substituted aroxy, alkylthio, substituted alkylthio, phenylthio, substituted phenylthio, arylthio, substituted arylthio, cyano, isocyano, substituted isocyano, carbonyl, substituted carbonyl, carboxyl, substituted carboxyl, amino, substituted amino, amido, substituted amido, sulfonyl, substituted sulfonyl, sulfonic acid, phosphoryl, substituted phosphoryl, phosphonyl, substituted phosphonyl, polyaryl, substituted polyaryl, C_3-C_{20} cyclic, substituted C_3-C_{20} cyclic, heterocyclic, substituted heterocyclic, aminoacid, peptide, and polypeptide groups.

Heteroatoms, such as nitrogen, may have hydrogen substituents and/or any permissible substituents of organic compounds described herein that satisfy the valences of the heteroatoms. It is understood that "substitution" or "substituted" includes the implicit proviso that such substitution is in accordance with permitted valence of the substituted atom and the substituent, and that the substitution results in a stable compound, i.e. a compound that does not spontaneously undergo transformation such as by rearrangement, cyclization, elimination, etc.

"Polymer", as used herein, refers to a molecule containing more than 10 monomer units.

"Water-soluble", as used herein, generally means at least 50, 75, 100, 125, 150, 200, 225, or 250 g is soluble in 1 L of water at 25° C.

II. Formulations

The formulations and methods disclosed herein are concerned with treating keratin in hair, skin, or nails. In one embodiment, the methods relate to strengthening and/or repairing hair after it has undergone a coloring treatment or after or during a permanent wave treatment. Additionally, the formulations may reduce or prevent hair damage due to hair coloring and/or bleaching processes.

A. Formulations

The formulations contain one or more polyfunctional compounds (also referred to herein as "active agents").

The active agents can be combined with one or more pharmaceutically acceptable carriers and/or excipients that are considered safe and effective to human hair and/or human scalp, and may be administered to an individual's hair without causing undesirable biological side effects, such as burning, itching, and/or redness, or similar adverse reactions. The formulations may further contain an excipient that renders the formulations neutral pH, or a pH ranging from about pH 3 to about pH 12, preferably from pH 5 to pH 8.

The active agent is typically present in an amount ranging from about 0.01 wt % to about 50 wt % of the formulation, preferably from about 1 wt % to about 25 wt % of the formulation, more preferably from about 1 wt % to about 15 wt %, most preferably from about 1 wt % to about 10 wt %. Typically, the active agent may be present in an amount ranging from about 0.5 to about 3 wt % of the formulation, or from about 1 to about 3 wt % of the formulation.

The active agent is stable in aqueous solution for a period of at least 2, 3, 4, 5, 6, 8, 9, 10, 11, or 12 months or longer at pH of 6 to 8 and a temperature of about 25-30° C., preferably about 25° C. "Stable" as used herein with respect to shelf-life means that at least 40, 45, 50, 55, 60, 65, 70, 75, 80, 85, 90, or 95% of the compound is unchanged over the specified period.

a. Active Agents

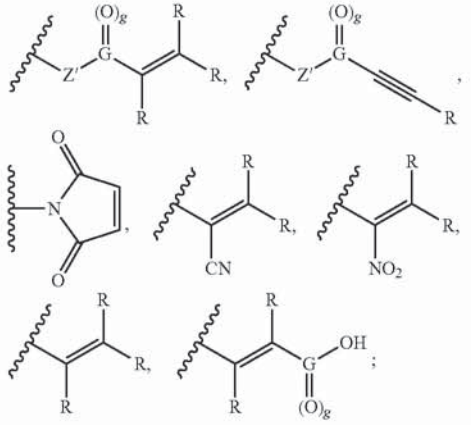
The active agent is a polyfunctional compound that may contain ionizable functional groups capable of forming ionic bonds and functional groups capable of forming a covalent bond with a thiol. Suitable ionizable functional groups include, but are not limited to, acidic groups such as carboxylic acids, sulfonic acids, phosphonic acids, and basic groups, such as amines. Suitable functional groups capable of forming a covalent bond with a thiol include, but are not limited to, Michael acceptors, alkyl halides or sulfonate esters.

The active agent may have the following Formula I:

$$(B)_m\text{-}Z\text{-}(A)_n \qquad \text{Formula I}$$

wherein Z is a linker or is absent, m and n are each an integer independently selected from 0-6, provided that m+n is at least 2, B is a functional group capable of forming a covalent bond with a thiol, and A is an ionizable functional group. In some embodiments, ionizable group A can be independently selected from the group consisting of: —COOH, —SO_3H, —PO_3H_2, and —$N(R^1)_2$; wherein R^1 is independently selected from the group consisting of a hydrogen, alkyl, alkenyl, alkynyl, cycloalkyl, aryl, heterocycloalkyl and heteroaryl groups; wherein each R^1 is independently unsubstituted or substituted with one or more substituents. In some other embodiments, ionizable group A can be an ionic group, such as —$N^+(R^1)_3$. In some preferred embodiments, each R^1 is independently selected from a methyl, ethyl, or isopropyl group.

Exemplary active agents according to Formula I may contain thiol reactive functional groups, as group B, for example, such as those shown in the following moieties:



wherein R is independently selected from hydrogen, $C_{1\text{-}6}$ alkyl, aryl, or an ionizable functional group; Z' is oxygen (O), NH, or is absent; and G is carbon (C) and g is 1, or G is sulfur (S) and g is 2.

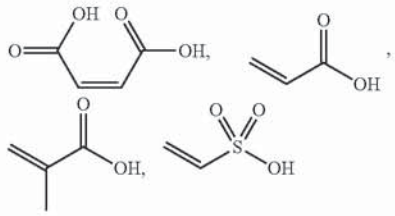
The linker Z, when present, can be or can contain an alkyl, alkenyl, cycloalkyl, cycloalkenyl, aryl, heterocycloalkyl or heteroaryl group. One or more of the carbon atoms in the alkyl, alkenyl, cycloalkyl, cycloalkenyl, and aryl groups can be substituted with a heteroatom, yielding, for instance, an ether or alkylamine-containing linker.

The linker Z may optionally be substituted with one or more substituents, which may be the same or different, including hydrogen, halogen, cyano, alkoxy, alkyl, alkenyl, cycloalkyl, cycloalkenyl, aryl, heterocycloalkyl, heteroaryl, amine, hydroxy, oxo, formyl, acyl, carboxylic acid (—COOH), —$C(O)R^1$, —$C(O)OR^1$, carboxylate (—COO—), primary amide (e.g., —$CONH_2$), secondary amide (e.g., —$CONHR_{11}$), —$C(O)NR^1R^2$, —NR^1R^2, —$NR^1S(O)_2R^2$, —$NR^1C(O)R^2$, —$S(O)_2R^2$, —SR^1, and —$S(O)_2NR^1R^2$, sulfinyl group (e.g., —SOR_1), and sulfonyl group (e.g., —$SOOR_1$); wherein R^1 and R^2 may each independently be hydrogen, alkyl, alkenyl, alkynyl, cycloalkyl, aryl, heterocycloalkyl and heteroaryl; wherein each of R^1 and R^2 is optionally independently substituted with one or more substituents selected from the group consisting of halogen, hydroxyl, oxo, cyano, nitro, amino, alkylamino, dialkylamino, alkyl optionally substituted with one or more halogen or alkoxy or aryloxy, aryl optionally substituted with one or more halogen or alkoxy or alkyl or trihaloalkyl, heterocycloalkyl optionally substituted with aryl or heteroaryl or oxo or alkyl optionally substituted with hydroxyl, cycloalkyl optionally substituted with hydroxyl, heteroaryl optionally substituted with one or more halogen or alkoxy or alkyl or trihaloalkyl, haloalkyl, hydroxyalkyl, carboxy, alkoxy, aryloxy, alkoxycarbonyl, aminocarbonyl, alkylaminocarbonyl and dialkylaminocarbonyl.

In certain preferred embodiments, the linker Z is a $C_{1\text{-}10}$ alkyl group which may be unsubstituted or substituted one or more times by oxo, hydroxyl, carboxyl, amido or amino. Preferably, the linker Z is a $C_{1\text{-}4}$ alkyl group. The alkyl group may be linear or branched. The alkyl group may also be

interrupted one or more times by a heteroatom selected from oxygen, sulfur and nitrogen. An example of such a dicarboxylic acid having a heteroatom interruption is thiodipropionic acid. In other embodiments, the alkyl group may contain one or more double or triple bonds.

In some embodiments, the active agent of Formula I has one of the following structures:



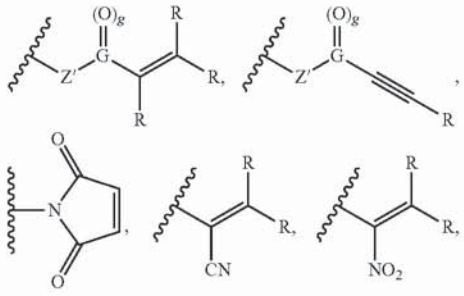
or is a simple salt of these structures.

In certain other embodiments, the active agent may have the following Formula II:

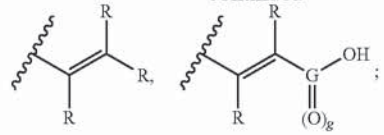
$$(B)_m—Z-(A)_n-(C)_o \qquad \text{Formula II}$$

wherein Z is a linker or is absent, m and n are each an integer independently selected from 0-6, provided that m+n is at least 2, B is a functional group capable of forming a covalent bond with a nucleophile, such as but not limited to a thiol or amine group, A is an ionizable functional group as defined above, and C contains an ionic group and a functional group which is also capable of forming a covalent bond with a nucleophile, such as but not limited to a thiol or amine group, and which has a charge opposite to that of ionizable group A. Group C is ionically bonded (denoted by dashed line) to group A. For ionic group C, o is an integer value independently selected from 0-6, such that the sum of charges of group C and ionizable group A is zero. In some embodiments, ionizable group A can be independently selected from the group consisting of: —COOH, $—SO_3H$, $—PO_3H_2$, and $—N(R^1)_2$; wherein R^1 is independently selected from the group consisting of a hydrogen, alkyl, alkenyl, alkynyl, cycloalkyl, aryl, heterocycloalkyl and heteroaryl groups; wherein each R^1 is independently unsubstituted or substituted with one or more substituents. In some other embodiments, ionizable group A can be an ionic group such as $—N^+(R^1)_3$. In some preferred embodiments, each R^1 is independently selected from a methyl, ethyl, or isopropyl group.

The active agents according to Formula II may contain thiol reactive functional groups as group B, for example, such as those shown in the following moieties:



-continued



wherein R is independently selected from hydrogen, C_{1-6} alkyl, aryl, or an ionizable functional group; Z' is oxygen (O), NH, or is absent; and G is carbon (C) and g is 1, or G is sulfur (S) and g is 2.

The linker Z, when present, can be or can contain an alkyl, alkenyl, cycloalkyl, cycloalkenyl, aryl, heterocycloalkyl or heteroaryl group. One or more of the carbon atoms in the alkyl, alkenyl, cycloalkyl, cycloalkenyl, and aryl groups can be substituted with a heteroatom, yielding, for instance, an ether or alkylamine-containing linker.

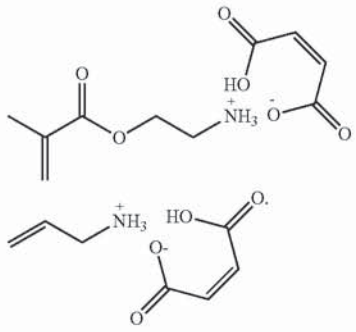
The linker Z may optionally be substituted with one or more substituents, which may be the same or different, including hydrogen, halogen, cyano, alkoxy, alkyl, alkenyl, cycloalkyl, cycloalkenyl, aryl, heterocycloalkyl, heteroaryl, amine, hydroxy, oxo, formyl, acyl, carboxylic acid (—COOH), $—C(O)R^1$, $—C(O)OR^1$, carboxylate (—COO—), primary amide (e.g., $—CONH_2$), secondary amide (e.g., $—CONHR^1$), $—C(O)NR^1R^2$, $—NR^1R^2$, $—NR^1S(O)_2R^2$, $—NR^1C(O)R^2$, $—S(O)_2R^2$, $—SR^1$, and $—S(O)_2NR^1R^2$, sulfinyl group (e.g., $—SOR_1$), and sulfonyl group (e.g., $—SOOR^1$); wherein R^1 and R^2 may each independently be hydrogen, alkyl, alkenyl, alkynyl, cycloalkyl, aryl, heterocycloalkyl and heteroaryl; wherein each of R^1 and R^2 is optionally independently substituted with one or more substituents selected from the group consisting of halogen, hydroxyl, oxo, cyano, nitro, amino, alkylamino, dialkylamino, alkyl optionally substituted with one or more halogen or alkoxy or aryloxy, aryl optionally substituted with one or more halogen or alkoxy or alkyl or trihaloalkyl, heterocycloalkyl optionally substituted with aryl or heteroaryl or oxo or alkyl optionally substituted with hydroxyl, cycloalkyl optionally substituted with hydroxyl, heteroaryl optionally substituted with one or more halogen or alkoxy or alkyl or trihaloalkyl, haloalkyl, hydroxyalkyl, carboxy, alkoxy, aryloxy, alkoxycarbonyl, aminocarbonyl, alkylaminocarbonyl and dialkylaminocarbonyl.

In certain preferred embodiments, the linker Z is a C_{1-10} alkyl group which may be unsubstituted or substituted one or more times by oxo, hydroxyl, carboxyl, amido or amino. Preferably, the linker Z is a C_{1-4} alkyl group. The alkyl group may be linear or branched. The alkyl group may also be interrupted one or more times by a heteroatom selected from oxygen, sulfur and nitrogen. An example of such a dicarboxylic acid having a heteroatom interruption is thiodipropionic acid. In other embodiments, the alkyl group may contain one or more double or triple bonds.

Group C is an ionic group ionically bonded to ionizable group A and contains at least one thiol reactive selected from a Michael acceptor, a succinimidyl-containing group, a maleimido-containing group, azlactone, a benzoxazinone derivative, vinyl sulfone, vinyl sulfoximine, vinyl sulfonate, vinyl phosphonate, benzoxazinone, isocyanate, epoxide, an electrophilic moiety containing a leaving group, an electrophilic thiol acceptor, acrylic or acrylate group, a methacrylic or methacrylate group, a styrene group, an acryl amide group, a methacryl amide group, a maleate group, a fumarate group, an itaconate group, a vinyl ether group, an allyl ether group, an allyl ester group, a vinyl ester group, a sulfonate group, a phosphonate group, a sulfoxide group, a sulfona-

mide group, a sulfinimide group, a sulfinamide group, a sulfonimidate group, or a sulfonimidamide group.

In some embodiments, the active agent of Formula II has one of the following structures:



or

b. Excipients

The formulations typically contain one or more cosmetically acceptable excipients. Cosmetically acceptable excipients include, but are not limited to preservatives, antioxidants, chelating agents, sunscreen agents, vitamins, dyes, hair coloring agents, proteins, amino acids, natural extracts such as plant extracts, humectants, fragrances, perfumes, oils, emollients, lubricants, butters, penetrants, thickeners, viscosity modifiers, polymers, resins, hair fixatives, film formers, surfactants, detergents, emulsifiers, opacifying agents, volatiles, propellants, liquid vehicles, carriers, salts, pH adjusting agents (e.g., citric acid), neutralizing agents, buffers, hair conditioning agents, anti-static agents, anti-frizz agents, anti-dandruff agents, absorbents, and combinations thereof.

The formulations typically contain at least two cosmetically acceptable excipients. In some forms, the formulations contain the active agent, water, and optionally a preservative and/or fragrance.

The formulation for treating hair may be in any suitable physical form. Suitable forms include, but are not limited to low to moderate viscosity liquids, lotions, milks, mousses, sprays, gels, creams, shampoos, conditioners, and the like. Suitable excipients, such as those listed above, are included or excluded from the hair care formulation depending on the form of use of the formulation (e.g., hair spray, cream, conditioner, or shampoo).

The pharmaceutical excipient is typically present in an amount ranging from about 10 wt % to about 99.99 wt % of the formulation, preferably about 40 wt % to about 99 wt %, more preferably from about 80 wt % to about 99 wt %.

i. Surfactants

Surfactants are surface-active agents that are able to reduce the surface tension of water and cause the hair formulation to slip across or onto the skin or hair. Surfactants also include detergents and soap. The surfactants may be amphoteric, anionic, or cationic. Suitable surfactants that may be used in the formulation include, but are not limited to, 3-aminopropane sulfonic acid, almond amide, almond amidopropyl betaine, almond amidopropylamine oxide, aluminum hydrogenated tallow glutamate, aluminum lanolate, aminoethyl sulfate, aminopropyl lauryl glutamine, ammonium C_{12-15} alkyl sulfate, ammonium C_{12-15} pareth sulfate, ammonium C_{12-16} alkyl sulfate, ammonium C_{9-10} perfluoroalkylsulfonate, ammonium capryleth sulfate, ammonium capryleth-3 sulfate, ammonium monoglyceride sulfate, ammonium sulfate, ammonium isothionate, ammonium cocoyl sarcosinate, ammonium cumene sulfonate, ammonium dimethicone copolyol sulfate, ammonium dodecylbenzenesulfonate, ammonium isostearate, ammonium laureth sulfate, ammonium laureth-12 sulfate, ammonium laureth-5 sulfate, ammonium laureth-6 carboxylate, ammonium laureth-7 sulfate, ammonium laureth-8 carboxylate, ammonium laureth-9 sulfate, ammonium lauroyl sarcosinate, ammonium lauryl sulfate, ammonium lauryl sulfosuccinate, ammonium myreth sulfate, ammonium myristyl sulfate, ammonium nonoxynol-30 sulfate, ammonium nonoxynol-4 sulfate, ammonium oleate, ammonium palm kernel sulfate, ammonium polyacrylate, ammonium stearate, ammonium tallate, ammonium xylene sulfonate, ammonium xylene sulfonate, amp-isostearoyl gelatin/keratin amino acids/lysine hydroxypropyltrimonium chloride, amp-isostearoyl hydrolyzed collagen, apricot kernel oil PEG-6 esters, apricot amide, apricot amidopropyl betaine, arachideth-20, avocadamide, avocadamidopropyl betaine, babassuamide, babassuamidopropyl betaine, babassuamidopropylamine oxide, behenalkonium chloride, behenamide, behenamide, behenamidopropyl betaine, behenamine oxide, sodium laureth sulfate, sodium lauryl sulfate, a polyoxyether of lauryl alcohol or ceteareth-20, or combinations thereof.

Suitable anionic surfactants include, but are not limited to, those containing carboxylate, sulfonate and sulfate ions. Examples of anionic surfactants include sodium, potassium, ammonium of long chain alkyl sulfonates and alkyl aryl sulfonates such as sodium dodecylbenzene sulfonate; dialkyl sodium sulfosuccinates, such as sodium dodecylbenzene sulfonate; dialkyl sodium sulfosuccinates, such as sodium bis-(2-ethylthioxyl)-sulfosuccinate; and alkyl sulfates such as sodium lauryl sulfate. Cationic surfactants include, but are not limited to, quaternary ammonium compounds such as benzalkonium chloride, benzethonium chloride, cetrimonium bromide, stearyl dimethylbenzyl ammonium chloride, polyoxyethylene and coconut amine. Examples of nonionic surfactants include ethylene glycol monostearate, propylene glycol myristate, glyceryl monostearate, glyceryl stearate, polyglyceryl-4-oleate, sorbitan acylate, sucrose acylate, PEG-150 laurate, PEG-400 monolaurate, polyoxyethylene monolaurate, polysorbates, polyoxyethylene octylphenylether, PEG-1000 cetyl ether, polyoxyethylene tridecyl ether, polypropylene glycol butyl ether, Poloxamer 401, stearoyl monoisopropanolamide, and polyoxyethylene hydrogenated tallow amide. Examples of amphoteric surfactants include sodium N-dodecyl-.beta.-alanine, sodium N-lauryl-β-iminodipropionate, myristoamphoacetate, lauryl betaine and lauryl sulfobetaine.

More than one surfactant may be included in the formulation.

The surfactants are optionally included in an amount ranging from about 0.1% to about 15% by weight of the formulation, preferably about 1% to about 10% by weight of the formulation.

ii. Emollients

Emollient refers to a material that protects against wetness or irritation, softens, soothes, coats, lubricates, moisturizes, protects, and/or cleanses the skin. Suitable emollients for use in the formulations include, but are not limited to, a silicone compound (e.g., dimethicone, cyclomethicone, dimethicone copolyol or a mixture of cyclopentasiloxane and dimethicone/vinyldimethicone cross polymer, cyclopentasiloxane polysilicone), polyols such as sorbitol, glycerin, propylene glycol, ethylene glycol, polyethylene glycol, caprylyl glycol, polypropylene glycol, 1,3-butane diol, hexylene glycol, isoprene glycol, xylitol; ethylhexyl palmitate; a triglyceride such as caprylic/capric triglyceride and fatty acid ester such

as cetearyl isononanoate or cetyl palmitate. In a specific embodiment, the emollient is dimethicone, amidodimethicone, dimethiconol, cyclopentasiloxane, potassium dimethicone PEG-7 panthenyl phosphate, or combinations thereof. More than one emollient may be included in the formulation.

The emollient is optionally included in an amount ranging from about 0.5% to about 15% by weight of the formulation, preferably from about 1% to about 10% by weight of the formulation.

iii. Emulsifiers

The formulation may also contain one or more emulsifiers. Suitable emulsifiers include, but are not limited to, copolymers of an unsaturated ester and styrene sulfonate monomer, cetearyl alcohol, glyceryl ester, polyoxyethylene glycol ether of cetearyl alcohol, stearic acid, polysorbate-20, ceteareth-20, lecithin, glycol stearate, polysorbate-60, polysorbate-80, or combinations thereof. More than one emulsifier may be included in the formulation.

The emulsifier is optionally included in an amount ranging from about 0.05%-15% by weight of the formulation, preferably from about 0.1%-10% by weight of the formulation.

iv. Preservatives

One or more preservatives may be included in the formulation. Suitable preservatives include, but are not limited to, glycerin containing compounds (e.g., glycerin or ethylhexylglycerin or phenoxyethanol), benzyl alcohol, parabens (methylparaben, ethylparaben, propylparaben, butylparaben, isobutylparaben, etc.), sodium benzoate, ethylenediamine-tetraacetic acid (EDTA), potassium sorbate, and/or grapefruit seed extract, or combinations thereof. More than one preservative may be included in the formulation. Other preservatives are known in the cosmetics industries and include salicylic acid, DMDM Hydantoin, Formaldeahyde, Chlorphenism, Triclosan, Imidazolidinyl Urea, Diazolidinyl Urea, Sorbic Acid, Methylisothiazolinone, Sodium Dehydroacetate, Dehydroacetic Acid, Quaternium-15, Stearalkonium Chloride, Zinc Pyrithione, Sodium Metabisulfite, 2-Bromo-2-Nitropropane, Chlorhexidine Digluconate, Polyaminopropyl biguanide, Benzalkonium Chloride, Sodium Sulfite, Sodium Salicylate, Citric Acid, Neem Oil, Essential Oils (various), Lactic Acid, and Vitamin E (tocopherol).

The preservative is optionally included in an amount ranging from about 0.1% to about 5% by weight of the formulation, preferably from about 0.3% to about 3% by weight of the formulation. Preferably, the formulations are paraben free.

v. Conditioning Agents

One or more conditioning agents may be included in the formulation. Suitable conditioning agents include, but are not limited to, silicone-based agents (e.g., silicone quaternium-8), panthenol, hydrolyzed wheat and/or soy protein, amino acids (e.g. wheat amino acids), rice bran wax, meadowfoam seed oil, mango seed oil, grape seed oil, jojoba seed oil, sweet almond oil, hydroxyethyl behenamidopropyl dimonium chloride, aloe leaf extract, aloe barbadensis leaf juice, phytantriol, panthenol, retinyl palmitate, behentrimonium methosulfate, cyclopentasiloxane, quaternium-91, stearamidopropyl dimethylamine, and combinations thereof.

The conditioning agent(s) is optionally included in an amount ranging from about 0.1% to about 5% by weight of the formulation, preferably from about 0.3% to about 3% by weight of the formulation.

vi. Diluents

Diluent, as used herein, refers to a substance(s) that dilutes the active agent. Water is the preferred diluent. The formulation typically contains greater than one percent (by wt) water, preferably greater than five percent (by wt) water, more preferably greater than 50% (by wt) water, and most preferably greater than 80% (by wt) water. Alcohols, such as ethyl alcohol and isopropyl alcohol, may be used at low concentrations (about 0.5% by weight of the formulation) to enhance hair penetration and/or reduce odor.

vii. Viscosity Modifying Agents

The formulations may contain one or more viscosity modifying agents, such as viscosity increasing agents. Classes of such agents include, but are not limited to, viscous liquids, such as polyethylene glycol, semisynthetic polymers, such as semisynthetic cellulose derivatives, synthetic polymers, such as carbomers, poloxamers, and polyethyleneimines (e.g., PEI-10), naturally occurring polymers, such as acacia, tragacanth, alginates (e.g., sodium alginate), carrageenan, vegetable gums, such as xanthan gum, petroleum jelly, waxes, particulate associate colloids, such as bentonite, colloidal silicon dioxide, and microcrystalline cellulose, surfactants, such as PPG-2 hydroxyethyl coco/isostearamide, emulsifiers, such as disteareth-75 IPDI, and salts, such as sodium chloride, and combinations thereof.

viii. Antioxidants

The formulation may contain one or more antioxidants. Examples include, but are not limited to, tocopheryls, BHT, ascorbic acid, *camellia sinensis* leaf extract, ascorbyl palmitate, magnesium ascorbyl phosphate, carotenoids, resveratrol, triethyl citrate, arbutin, kojic acid, tetrahexydecyl ascorbate, superoxide dismutase, zinc, sodium metabisulfite, lycopene, ubiquinone, and combinations thereof.

ix. Opacifying Agents

The formulation may contain one or more opacifying agents. Opacifying agents are added to the formulations to make it opaque. Suitable opacifying agents include, but are not limited to, glycol distearate and ethoxylated fatty alcohols.

c. Forms of the Formulation

i. Sprays

The formulation may be in the form of a spray. The spray typically includes the active agent and a cosmetically acceptable carrier. In some embodiments, the carrier is water or a water and alcohol mixture. The spray formulation optionally includes an antioxidant, sunscreen agent, vitamin, protein, peptide, plant extract, humectant, oil, emollient, lubricant, thickener, hair conditioning agent, polymer, and/or surfactant. Preferably, the spray formulation includes a preservative. In some embodiments, the formulation includes a fragrance. In some embodiments, the formulation includes a surfactant. In some embodiments, the formulation contains water, fragrance, a preservative, and an active agent. In some embodiments, the formulation contains water, fragrance, a preservative, and an active agent. In some embodiments, the formulation contains water, a preservative, fragrance, an active agent, and an anti-static agent. In some embodiments, the formulation contains water, a preservative, fragrance, an active agent, and a hair conditioning agent. In some embodiments, the formulation contains water, a preservative, fragrance, an active agent, and a surfactant.

The hair spray formulations may be dispensed from containers that include aerosol dispensers or pump spray dispensers. Such dispensers are known in the art and are commercially available from a variety of manufacturers.

Propellant

When the hair spray formulation is dispensed from a pressurized aerosol container, a propellant may be used to force the formulation out of the container. Suitable propel-

lants include, but are not limited to, a liquefiable gas or a halogenated propellant. Examples of suitable propellants include dimethyl ether and hydrocarbon propellants such as propane, n-butane, iso-butane, CFCs, and CFC-replacement propellants. The propellants may be used singly or admixed.

The amount of propellant may range from about 10% to about 60% by weight of the formulation. The propellant may be separated from the hair repair formulation as in a two compartment container. Other suitable aerosol dispensers are those characterized by the propellant being compressed air, which can be filled into the dispenser using a pump or equivalent device prior to use. Conventional non-aerosol pump spray dispensers, i.e., atomizers, may also be used to apply the formulation to the hair.

ii. Conditioners

The formulation may be in the form of a conditioner. The conditioner typically includes the active agent in a suitable carrier. Additionally, the conditioner may include cationic polymers derived from polysaccharides, for example cationic cellulose derivatives, cationic starch derivatives, cationic guar derivatives and cationic locust bean gum derivatives, synthetic cationic polymers, mixtures or combinations of these agents. The formulation may comprise other synthetic or natural polymers or polymers derived from biological preparation processes, which are functionalized, where appropriate, for example with cationic or neutral groups. These polymers may have a stabilizing or strengthening action on the formulation, and/or a conditioning action (deposition on the surface of the skin or the hair).

The active agent may be included in any suitable concentration. Typical concentrations of active agent in the conditioner range from small amounts such as approximately 0.01% (by wt), preferably at least 0.1% (by wt), to large amounts, such as up to 50% (by wt). Preferably the conditioner contains the active agent in a concentration ranging from 0.1% (by wt) to 5% (by wt), more preferably from 0.1% wt to 3% (by wt). While greater concentrations of active agent could be present in the conditioner, they are generally not needed to achieve the desired results.

iii. Shampoos

The hair repair formulation may be in the form of a shampoo. The shampoo typically includes the active agent in a suitable carrier. The active agent may be included in any suitable concentration. Typical concentrations of the active agent in the shampoo range from small amounts such as approximately 0.01% (by wt), preferably at least 0.1% (by wt), to large amounts, such as up to 50% (by wt). Preferably the shampoo contains the active agent in a concentration ranging from 0.1% (by wt) to 5% (by wt), more preferably from 0.1% (by wt) to 3% (wt). While greater concentrations of active agent could be present in the shampoo, they are generally not needed to achieve the desired results.

Additionally, the shampoo may include from about 0.5% to about 20% by weight of a surfactant material. Surfactants utilized in shampoo compositions are well-known in the art and are disclosed, for example, in U.S. Pat. No. 6,706,258 to Gallagher et al. and U.S. Pat. No. 7,598,213 to Geary et al.

iv. Creams, Lotions, Gels, and Polish

The hair, skin, or nail repair formulation may be in the form of a cream, lotion, gel, or polish. The cream, lotion, gel, or polish typically includes the active agent in a suitable carrier. The active agent may be included in any suitable concentration. Typical concentrations of the active agent in the cream, lotion, gel, or polish range from small amounts such as approximately 0.01% (by wt), preferably at least 0.1% (by wt), to large amounts, such as up to 50% (by wt). Preferably the cream or lotion contains the active agent in a concentration ranging from 0.1% (by wt) to 5% (by wt), more preferably from 0.1% (by wt) to 3% (by wt). While greater concentrations of active agent could be present in the cream or lotion, they are generally not needed to achieve the desired results.

Additionally, the formulation, depending on use, may include an oil, a hair conditioning agent, and/or a thickening agent. The cream, lotion, gel, or polish may also include a fragrance, a plant extract, and/or a surfactant. The cream, lotion, gel, or polish may be packaged in a tube, tub, bottle, or other suitable container.

v. Liquid Active Agent Formulations

In some embodiments, a liquid active agent formulation is provided, which is mixed at the time of use with a second formulation, such as a coloring or highlighting formulation. In these embodiments, the liquid active agent formulation may contain any suitable concentration of active agent in a suitable carrier, typically a diluent, such as described above. The concentration of the active agent is suitable to provide a mixture with the appropriate final volume and final concentration of active agent.

For example, a liquid active agent formulation can contain a concentration of active agent ranging from about 5% (by wt) to about 50% (by wt) or greater. In a preferred embodiment, the liquid active agent formulation contains about 20% (by wt) active agent.

For highlighting applications, prior to use, a sufficient volume of a liquid active agent formulation is mixed with a sufficient volume of a highlighting formulation to form a highlighting mixture having the desired concentration of active agent. Typical concentrations of the active agent in the highlighting mixture range from small amounts, such as approximately at least 0.01% (by wt), preferably at least 0.1% (by wt), to large amounts, such as up to 50% (by wt). Preferably the highlighting mixture contains the active agent in a concentration ranging from 0.1% (by wt) to 5% (by wt), more preferably from 0.1% (by wt) to 3% (wt). While greater concentrations of active agent could be present in the highlighting mixture, they are generally not needed to achieve the desired results.

III. Methods of Use

A. Treatment of Hair with Coloring Agents

a. Apply the Coloring Formulation to the Hair

The coloring formulation is generally applied to an individual's hair following normal hair coloring procedures that are known to those skilled in the art. Typically, hair color treatments include two complementary processes: applying a bleaching formulation to bleach the hair's natural pigment and/or other artificial pigments present in the hair, and diffusion of dye precursors into the hair, followed by coupling reactions that result in the formation of chromophores within the hair shaft, which are too large to diffuse out of the hair. The bleaching formulation typically contains a bleaching agent to lighten the hair and produce free thiol groups. The hair coloring formulation may be a highlighting formulation, such as formed by mixing bleach powder and developer. More complex colors may contain several precursors and many couplers, and may involve multiple reactions.

The dye precursors may contain several ingredients, each with different functions. The first ingredient is usually an alkalizing agent (usually ammonia and/or an ammonia substitute, such as monoethanolamine [MEA]). The alkalizing agent serves a number of roles in the hair colorant process including swelling the hair fiber to aid in diffusion of the dye precursors. The dye precursors generally include p-diamines and p-aminophenols. Precursors are oxidized to active intermediates once they have penetrated the hair shaft. Interme-

diates then react with color couplers to create wash resistant dyes. More specifically, the intermediates, in the presence of an oxidant, couple with another oxidation dye intermediate molecule to form a large fused ring color compound within the hair shaft. The precursor intermediate should penetrate the hair shaft prior to the coupling reaction since the fused ring product is too large to penetrate the hair shaft. Couplers modify the color produced by the oxidation of precursor compounds. The primary difference between demi-permanent and permanent products is the alkalizing agent and the concentration of peroxide. The cuticle does not swell as greatly with demi-permanent dyes, making dye penetration less efficient compared to permanent coloring products.

Several coloring formulations use a reducing agent, such as sodium bisulfate, to break disulfide bonds in the hair, allowing deeper penetration of the hair coloring dyes into the hair. Specifically, the method includes reducing some of the disulfide linkages of the cystine in the hair shafts to thiol groups while breaking hydrogen bonds. The reducing process changes the chemical and cosmetic characteristics of the hair, which are undesirable.

The hair dyeing process may be followed by a shampoo and conditioning treatment, a neutralizing rinse or an acid balanced shampoo containing in addition to cationic or amphoteric surfactants, cation-active emollients and quaternary polymers. Alternately, the hair dying process may be followed by application of the active agent formulations described herein, before a shampoo and/or conditioning treatment.

b. Apply the Active Agent Formulation to the Hair

The active agent formulation may be applied simultaneously with the hair coloring formulation or subsequently to the application of the hair coloring formulation. For example, the active agent formulation may be mixed with the hair coloring treatment and the mixture, containing both the active agent and the hair coloring treatment, may be applied to the hair.

Alternatively, subsequent to coloring the hair, the active agent formulation, or a formulation thereof is applied to the hair. Although the active agent is typically applied on the same day as the coloring treatment, it may be applied later such as within 1 to 2 weeks following treatment with the reducing agent. Typically, the amount of active agent formulation (or a mixture of the active agent formulation and the hair coloring formulation) applied is sufficient to saturate the hair. The active agent may be applied to the hair as a single application, or application of the active agent may be repeated one or more times. Typically, the amount of active agent formulation applied in each application is sufficient to saturate the hair. The volume of active agent formulation applied to the hair in each application may be about 1 to about 100 mL per person depending on their length and volume of hair. In some embodiments, application of the active agent could be repeated immediately (e.g. within 10 to 15 seconds) or approximately 1, 5, 7.5, 10, 12.5, 15, 17.5, or 20 minutes after the first application.

The active agent can be rinsed and shampooed from the hair immediately following application, for example within 10, 15, 25, 30, 45, or 60 seconds, or two, three, four, or five minutes after application. Alternatively, the active agent may be rinsed from the hair within about 30 minutes following application, preferably between about 5 minutes and about 20 minutes, more preferably about 10 minutes after application of the active agent to the hair, depending on hair type.

If the active agent formulation is combined with the hair coloring treatment and applied as a mixture to the hair, then the mixture remains on the hair as long as needed for the hair coloring treatment. Typically the mixture is applied for approximately 10 minutes. The mixture is removed from the hair in accordance with standard methods for hair coloring treatments, e.g., rinse and shampoo, approximately 10 minutes after applying the mixture.

The active agent formulation is rinsed from the hair after its application. The hair may be rinsed and subsequently washed immediately (e.g. within 10 to 15 seconds following application) after the final application of the active agent. Preferably, the hair is rinsed and/or washed about 10 minutes or later after the final application of the active agent, such as about 15 minutes to about 30 minutes, optionally about 20 minutes after repeated application of the active agent to the hair.

The active agents are generally washed from the individual's hair on the same day as they are applied. In contrast, traditional perms which use only hydrogen peroxide (and do not involve the addition of the active agent) are generally not washed for at least 48 hours following application (washing the hair prior to 48 hours following a traditional permanent treatment may result in significant loss in the amount of curl in the hair and/or cause damage to the hair).

The formulation described herein improves hair quality, such as appearance (e.g., sheen) and feel, and decreases hair breakage when the hair is subjected to treatments, such as coloring or permanent waving.

In some embodiments, hair breakage decreases by 5, 10, 15, 20, 25, 30, 35, 40, 45, or 50% or higher after treatment with the active agent compared to untreated hair from the same individual. Hair breakage is a significant problem encountered during coloring and other treatments.

B. Chemical Treatment of Hair with a Reducing Agent

In one embodiment, prior to treatment with the active agent, the hair has been subjected to a reducing agent used for waving (also referred to herein as hair perming or permanent waves), and/or curling of the hair.

a. Apply a Reducing Agent to the Hair

The first step in waving or curling hair is breaking the cysteine disulfide bonds to form free thiol moieties. The process for breaking the cysteine disulfide bonds is via application of a reducing agent. The process for applying the reducing agent involves following normal perming or hair straightening procedures that are known to those skilled in the art. For example, to perm hair, the hair is first washed and set on perm rods of various sizes. Second, a reducing agent, such as thioglycolate reducing solution or lotion is applied to the hair. The hair is allowed to set for a specified period of time, and then the thioglycolate solution is rinsed from the hair.

The application of hydrogen peroxide in this process is optional. In some processes, such as when treating previously chemically treated hair, hydrogen peroxide is generally not used. In other processes, such as when perming virgin hair, hydrogen peroxide may be added. In these embodiments, hydrogen peroxide is typically added after the reducing agent is rinsed out. Then the hydrogen peroxide is rinsed from the hair prior to adding the active agent.

b. Apply the Active Agent

Subsequent to the reducing treatment, one or more of the active agent, or a formulation thereof is applied to the hair. Although the agent is typically applied on the same day as treatment with the reducing agent, it may be applied later such as within 1 to 2 weeks following treatment with the reducing agent.

Typically, the amount of active agent formulation applied is sufficient to saturate the hair. The agent is generally rinsed and shampooed from the hair after the desired level of hair

waving or curling is achieved. In some embodiments, the active agent is rinsed from the hair immediately (e.g. within 10, 15, 25, 30, 45, or 60 seconds following application) following the final application of the active agent. Alternatively the hair may be rinsed and washed about within about 30 minutes following application, preferably between about 5 minutes and about 20 minutes, more preferably about 10 minutes after the final application of the active agent to the hair, depending on the hair type. The active agent can be rinsed from the hair within 10, 15, 25, 30, 45, 60 seconds from the hair after application, and still achieve a desired level of hair waving or curling.

The active agent may be applied to the hair as a single application, or application of the agent may be repeated one or more times. Typically, the amount of active agent formulation applied in each application is sufficient to saturate the hair. In some embodiments, the volume of active agent formulation applied to the hair in each application is about 1 to about 10 mL per perm rod. In some embodiments, application of the active agent could be repeated immediately (e.g. within 10 to 15 seconds) or approximately 1, 5, 7.5, 10, 12.5, 15, 17.5, or 20 minutes after the first application. In some embodiments, the second application is about 7 minutes to about 10 minutes after the first application.

The active agent is rinsed from the hair after its application. The hair may be rinsed and washed immediately (e.g. within 10 to 15 seconds following application) after final application of the active agent. Alternatively the hair may be rinsed and washed about 10 minutes or later after the final application of the active agent, such as about 15 minutes to about 30 minutes, preferably about 20 minutes after repeated application of the active agent to the hair.

The active agents are generally washed from the individual's hair on the same day as they are applied. In contrast, traditional perms which use only hydrogen peroxide (and do not involve the addition of the active agent) are generally not washed for at least 48 hours following application (washing the hair prior to 48 hours following a traditional permanent treatment may result in significant loss in the amount of curl in the hair and/or cause damage to the hair).

The formulations described herein can be applied to hair to improve hair quality, such as appearance (e.g., sheen) and feel, and decrease hair breakage when the hair is subjected to subsequent treatments, such as coloring.

In some embodiments, hair breakage decreases by 5, 10, 15, 20, 25, 30, 35, 40, 45, or 50% or higher after application of the active agent compared to untreated hair from the same individual. Hair breakage is a significant problem encountered during coloring and other treatments.

C. Treatment of Skin or Nails with the Active Agent

In one embodiment, a formulation containing one or more of the active agents is applied to the skin or nails. Application of the active agent formulation to skin or nails can help repair damaged disulfide bonds due to natural wear and tear or natural aging.

In some embodiments the active agent formulation is in the form of a cream or lotion, which is suitable for application to the skin or nails. In other embodiments, the active agent formulation is in the form of a gel or polish, which is suitable for application to the nails. Typically, the amount of active agent formulation applied is sufficient to treat the damaged keratin in the skin or nails. The active agent formulation may be applied to the skin or nails in a single application, or application of the formulation may be repeated one or more times, as needed, to achieve the desired effect of repairing keratin damage and/or strengthening the skin or nails.

IV. Kit

Kits for treating hair are provided. In one embodiment, the kit typically contains a first formulation for coloring hair. The hair coloring formulations typically include a reducing agent capable of reducing disulfide bonds in hair to produce free thiol groups. The kit also includes a second formulation containing an effective amount of the active agent.

The kit may further include a developer bottle, gloves, shampoo, conditioner, and/or an odor eliminator. Instructions for use of the kit are also typically provided.

Typically the kit contains more than one container (or more than one compartment in a given container) to ensure that the lightening agent (e.g., peroxides) or the coloring agent is stored separately from the active agent.

A. First Formulation

The first formulation in the kit can be a coloring treatment. The first formulation may be formulated as two or more components which may be mixed together before application to the hair. For example, the first formulation may be in the form of two components such as a dye precursor and an oxidant. Typically, the hair coloring formulation contains a reducing agent capable of reducing the disulfide bonds in hair and producing reduced free thiol groups. Suitable reducing agents include, but are not limited to, thioglycolic acid, thiolactic acid, dihydrolipoate, thioglycerol, mercaptopropionic acid, sodium bisulfite, ammonium bisulfide, zinc formaldehyde sulfoxylate, sodium formaldehyde sulfoxylate, sodium metabisulfite, potassium borohydride, pegylated thiols and hydroquinone. The amount of the reducing agent in the first formulation is sufficient to rupture a sufficient number of disulfide bonds for effective diffusion of the hair coloring ingredients as would be appreciated by one of skill in the art.

The components of the first formulation may differ depending on the hair coloring treatment desired (such as for semi-permanent, demi-permanent, or permanent hair color), the texture of the hair, the sensitivity of the user's skin, and such the like. Hair coloring formulations for different hair coloring treatment, hair texture, and hair sensitivity are known to those of skill in the art.

B. Active Agent Formulation

The second formulation contains one or more active agents in an effective amount. Suitable formulations containing the active agents are discussed above. The second formulation may be in any suitable form. Suitable forms include, but are not limited to, low to moderate viscosity liquids, lotions, milks, mousses, sprays, gels, creams, shampoos, conditioners, and the like. The second formulation will be present in a suitable container, which depends on the form of the formulation.

In one embodiment, the active agent formulation is provided as two or more separate ingredients. For example, the active agent may be provided as a dry powder in a sealed package and the excipient provided in a vial or other container. A suitable mixing container for the active agent and the excipient may be provided.

In some embodiments, the active agent formulation (or second formulation) is mixed with the first formulation (or hair coloring treatment), and the mixture is applied to the hair.

C. Other Materials in the Kit

The kit optionally contains shampoos and conditioners. Suitable shampoos and conditioners include, but are not limited to LIQWD® Hydrating Shampoo and LIQWD® Hydrating Conditioner.

The kit may further contain an odor eliminator. The odor eliminator can be incorporated into the first or second formulation, or a mixture thereof. Alternately, the odor eliminator is present in a suitable container for use before or after washing the second formulation from the hair. Some suitable odor eliminators are known to those of ordinary skill in the art.

It is understood that the disclosed method and formulations are not limited to the particular methodology, protocols, and reagents described as these may vary. It is also to be understood that the terminology used herein is for the purpose of describing particular embodiments only, and is not intended to limit the scope of the present invention which will be limited only by the appended claims.

EXAMPLES

Example 1

Color Retention and Texture of Colored Hair Treated with the Active Agent Formulation

General

Three hair samples were obtained from a human subject and cut in ½ inch wide wefts.

Coloring Formulation: The permanent hair coloring formulation was obtained from a L'OREAL® permanent hair coloring service (L'OREAL® MAJIREL® permanent color #10 with 20 volume peroxide).

Active Agent Formulation: Maleic acid, at a concentration of 200 mg in 10 g total solution (water) was used.

Methods

The hair samples were washed with a clarifying shampoo then towel dried. The samples were then colored with the L'OREAL® permanent hair color service, which was left on the hair samples for approximately 35-40 minutes.

The first color treated hair sample ("control") was subsequently rinsed and washed with LIQWD® Hydrating Shampoo and Conditioner five times before being photographed.

The active agent formulation was applied to the second and third color treated hair samples via a spray bottle and massaging using the fingers. The active agent formulation was left on the second hair sample for a period of about 1 minute and on the third sample for a period of about 10 minutes. The hair samples were subsequently rinsed, and then washed with LIQWD® Hydrating Shampoo and Conditioner five times before being examined.

Results:

The hair samples treated with the active agent formulation showed better color retention, more shine, and less frizz than the control. The hair samples treated with the active agent formulation felt smoother to the touch and combined with the lower frizz and added sheen gave an overall healthier appearance over the control.

Example 2

Comparison of Color Retention in Traditionally Permed Hair and Hair Permed Using the Active Agent Formulations

Method

A ½ inch wide weft of hair sample, obtained from a human subject, was washed with clarifying shampoo then towel dried. Ammonium thioglycolate or dithiothreitol was mechanically pulled through the hair with a wide and a fine toothcomb several times then left on the hair for 10 minutes to 1 hour. The hair was then rinsed for 30 seconds to 1 minute with water, and then towel dried.

The active agent formulation, described in Example 1 (Maleic acid in water), was then applied via a needle nose applicator drenching the hair and leaving it on for 7.5 minutes. This step was repeated, for a total of 15 minutes. The hair was then rinsed for 1-2 minutes, shampooed, and then conditioned with various salon shampoo and conditioner brands, including LIQWD® Hydrating Shampoo and Hydrating Conditioner.

A second sample of hair was straightened, as described above, but using hydrogen peroxide instead of the active agent formulation. The hair samples were washed and conditioned repeatedly.

Comparison of Hair Color:

After both hair samples were washed five times using LIQWD® Hydrating Shampoo and LIQWD® Hydrating Conditioner, the samples were examined for their color retention.

Results

The hair sample treated with the active agent formulation displayed a color closer in intensity to the hair sample prior to the first washing, compared to the hair treated with hydrogen peroxide.

Example 3

Comparison of Hair Treated with Highlighting Formulation Applied Simultaneously with Active Agent Formulation and Hair Treated with Highlighting Formulation Alone

The active agent formulation in Example 1 contained maleic acid at concentrations of 2.0 g in 10 g total solution (water).

Two swatches of human hair were tested. A sample was taken from the same head, 1 inch wide, and split in half. The color was medium brown and had been previously color treated with an unknown professional hair color.

Swatch 1, ½ inch wide and 8 inches long, was lightened with traditional highlighting ingredients mixed with the active agent formulation. 1 oz of Joico Verocolor Veroxide developer-20 volume was mixed with 1 oz Joico Verolight powder bleach to form the highlighting formulation. Then 9 mL of the active agent formulation was added to the highlighting formulation to form a mixture.

The mixture was applied on the Swatch 1 hair with an applicator brush as the hair lay on aluminum foil. The foil was then wrapped around the swatch and allowed to process for 35 minutes. The swatch was rinsed and shampooed one time.

Swatch 2, the control, ½ inch wide and 8 inches long, was lightened with traditional highlighting ingredients in the absence of the active agent formulation. 1 oz of Joico Verocolor Veroxide developer-20 volume was mixed with 1

oz Joico Verolight powder bleach to form a highlighting formulation with a creamy consistency.

The highlighting formulation was applied on the Swatch 2 hair with an applicator brush as the hair lay on aluminum foil. The foil was then wrapped around the swatch and allowed to process for 35 minutes. The swatch was rinsed and shampooed one time.

Results

A noticeable difference in hair quality between Swatch 1 and Swatch 2 was observed. Swatch 1 hair was softer, less frizzy, appeared hydrated, with more shine than the control, Swatch 2.

Both swatches were washed and conditioned 5 more times with the same noticeable benefits of Swatch 1 (treated with the mixture of highlighting formulation and active agent formulation) compared to the control, Swatch 2 (treated with highlighting formulation, alone).

Example 4

Comparison of Hair Treated with Bleaching Formulation Applied Simultaneously with Active Agent Formulation and Hair Treated with Bleaching Formulation Alone

General

Two hair samples were obtained from a human subject and cut in ½ inch wide wefts.

Methods

(1) 0.5 ounces of powder lightener (Clairol Professional, Basic White) and 0.5 ounces of conditioning cream developer (Redken, Blonde Icing) were combined to form a bleaching mixture. 3.5 g of 2-(methacryloyloxy)ethan-1-aminium (Z)-3-carboxyacrylate (12 wt % in water) was added to the bleaching mixture and thoroughly mixed with a brush.

(2) The bleaching mixture prepared was brushed onto the swatches of hair with a brush in order to thoroughly coat the strands of hair. The mixture coated hair was wrapped in aluminum paper and allowed to stand under ambient conditions for a period of two hours.

(3) After the two hour bleaching period the swatches of hair were washed with shampoo and the hair was subsequently allowed to air dry.

Results

A noticeable difference in hair quality between Swatch 1 and Swatch 2 was observed. Swatch 1 hair demonstrated no discernible breakage, great feel, and a healthy appearance while the control (treated with bleaching formulation, alone) showed some breakage, had a rough feel, and was frayed with an unhealthy appearance.

Example 5

Comparison of Hair Treated with Bleaching Formulation Applied Simultaneously with Active Agent Formulation and Hair Treated with Bleaching Formulation Alone

General

Two hair samples were obtained from a human subject and cut in ½ inch wide wefts.

Methods

(1) 0.5 ounces of powder lightener (Clairol Professional, Basic White) and 0.5 ounces of conditioning cream developer (Redken, Blonde Icing) were combined to form a bleaching mixture. 3.5 g of prop-2-en-1-aminium (Z)-3-carboxyacrylate (10 wt % in water) was added to the bleaching mixture and thoroughly mixed with a brush.

(2) The bleaching mixture prepared was brushed onto the swatches of hair with a brush in order to thoroughly coat the strands of hair. The mixture coated hair was wrapped in aluminum paper and allowed to stand under ambient conditions for a period of two hours.

(3) After the two hour bleaching period the swatches of hair were washed with shampoo and the hair was subsequently allowed to air dry.

Results

A noticeable difference in hair quality between Swatch 1 and Swatch 2 was observed. Swatch 1 hair demonstrated no discernible breakage, great feel, and a healthy appearance while the control (treated with bleaching formulation, alone) showed some breakage, had a rough feel, and was frayed with an unhealthy appearance.

Example 6

Comparison of Traditional Perm Versus Perm Using Maleic Acid

General

Hair samples were obtained from a human subject and cut in ½ inch wide wefts.

Reducing Agents: Ammonium thioglycolate (ATG) was obtained from a permanent wave kit manufactured by Zotos. 300 mg of Dithiothreitol in a 10 g solution was also used as the reducing agent.

Active Agent Formulation: Maleic acid at a concentration of 200 mg in 10 g total solution (water) was used.

Methods

Method for Perming Hair Using the Active Agent

The hair was washed with clarifying shampoo, towel dried, and then rolled around a perm rod. Ammonium thioglycolate or dithiothreitol was then applied to the hair and left on the hair for 10 minutes to 1 hour. The hair was then rinsed for 30 seconds to 1 minute and then blotted dry with a towel.

The active agent formulation was applied to the hair, via a needle nose applicator, drenching the hair. The active agent formulation was left on the hair for a period of about 7.5 minutes. The hair was drenched for a second time with the active agent formulation and left for a second 7.5 minutes, for a total of 15 minutes. The hair was then rinsed with water for about 1-2 minutes then unrolled from the perm rods. After the hair was removed from the perm rods, the hair was shampooed and conditioned with various salon shampoo and conditioner brands, including LIQWD® Hydrating Shampoo and Hydrating Conditioner. The washing and drying steps were repeated 40 times.

A second portion of hair was permed as described above, except, hydrogen peroxide was used instead of the active agent formulation.

Results

Both perms (utilizing the active agent formulation or hydrogen peroxide) showed only slight reduction in the overall curl after 40 cycles of washing and drying with the same shampoo and conditioner. However, the appearance and texture of the perm using the active agent formulation showed more sheen and less frizz compared to the perm using hydrogen peroxide.

Example 7

Comparison of Hair Breakage Due to Repeated Application of Traditional Perm and the Active Agent Formulation

Methods

Two hair samples were obtained. Both samples were treated with dithiothreitol or ammonium thioglycolate as described in Example 6. One of the hair samples was subsequently treated with the active agent formulation (Maleic acid in water), while the other was neutralized with hydrogen peroxide. The process was completed the same day for the hair treated with the active agent formulation. The process was completed in three days with hydrogen peroxide (traditional perm).

The procedure was repeated three times for each hair sample over a 48 hour time period.

Results

Upon visual inspections, the second hair sample treated with the active agent formulation showed little or no signs of breakage. However, the first hair sample treated with hydrogen peroxide showed significant breakage.

Example 8

Comparison of the Extent of Damage to Hair Previously Relaxed with a Japanese Relaxer

Methods

Two samples of hair, the first previously straightened with a Japanese relaxer (Yuko), and the second previously straightened with a no lye relaxer (African Pride Miracle Deep Conditioning) were obtained. The samples were treated as described in Examples 6 and 7 using the active agent formulation (Maleic acid in water).

Another hair sample, previously straightened with a no lye relaxer (African Pride Miracle Deep Conditioning) was obtained. The sample was treated with a traditional hair straightening perm (Zotos).

Results

The hair samples treated with the active agent formulation showed no noticeable damage. However, the sample treated with a traditional perm showed significant breaking, even during application.

Unless defined otherwise, all technical and scientific terms used herein have the same meanings as commonly understood by one of skill in the art to which the disclosed invention belongs. Publications cited herein and the materials for which they are cited are specifically incorporated by reference.

Those skilled in the art will recognize, or be able to ascertain using no more than routine experimentation, many equivalents to the specific embodiments of the invention described herein. Such equivalents are intended to be encompassed by the following claims.

We claim:

1. A method for bleaching hair comprising:

(a) mixing a bleach powder and a developer to form a bleaching formulation;

(b) mixing an active agent formulation comprising an active agent with the bleaching formulation to form a mixture, wherein the active agent is maleic acid; and

(c) applying the mixture to the hair;

wherein the active agent in the mixture is at a concentration ranging from about 0.1% by weight to about 50% by weight.

2. The method of claim **1**, wherein the active agent is present in an amount ranging from about 1 wt % to about 10 wt % of the active agent formulation.

3. The method of claim **1**, wherein the active agent is present in an amount ranging from about 0.5 to 3 wt % of the active agent formulation.

4. The method of claim **1**, wherein the active agent is present in an amount ranging from about 1 wt % to about 15 wt % of the active agent formulation.

5. The method of claim **1**, wherein the active agent is present in an amount ranging from about 0.1 wt % to about 5 wt % of the mixture.

6. The method of claim **1**, wherein the active agent is present in an amount ranging from about 0.1 wt % to about 3 wt % of the mixture.

7. The method of claim **1**, wherein the active agent formulation further comprises one or more excipients in an amount ranging from about 50 wt % to about 90 wt % of the active agent formulation.

8. The method of claim **1**, wherein the active agent formulation is in the form of a liquid.

9. The method of claim **1**, wherein step (c) is repeated one or more times.

10. The method of claim **1**, further comprising:

(d) rinsing, shampooing, or conditioning the hair, or a combination thereof, wherein step (d) occurs subsequent to step (c).

11. The method of claim **1**, wherein step (b) occurs at the time of use and prior to application of the mixture to the hair.

12. The method of claim **1**, further comprising:

(d) applying a second active agent formulation comprising maleic acid,

wherein step (d) occurs subsequent to step (c).

13. The method of claim **12**, wherein the second active agent formulation further comprises a conditioning agent.

14. The method of claim **13**, wherein following step (d) breakage of the hair is decreased by at least 5% compared to hair bleached with the bleaching formulation in the absence of the active agent.

15. The method of claim **13**, wherein following step (d) breakage of the hair is decreased by at least 10% compared to hair bleached with the bleaching formulation in the absence of the active agent.

16. The method of claim **13**, wherein following step (d) breakage of the hair is decreased by at least 20% compared to hair bleached with the bleaching formulation in the absence of the active agent.

17. The method of claim **13**, wherein following step (d) breakage of the hair is decreased by at least about 40% compared to hair bleached with the bleaching formulation in the absence of the active agent.

18. The method of claim **13**, wherein following step (d) breakage of the hair is decreased by at least 50% compared to hair bleached with the bleaching formulation in the absence of the active agent.

19. The method of claim **13**, wherein the conditioning agent in the second active agent formulation is present in an amount ranging from about 0.1 to about 5% by weight of the second active agent formulation.

20. The method of claim **19**, wherein the conditioning agent in the second active agent formulation comprises behentrimonium methosulfate and stearamidopropyl dimethylamine.

21. The method of claim **19**, wherein the second active agent formulation is in the form of a cream.

22. The method of claim **21**, wherein the second active agent formulation comprises water, glycerin, propylene gly-

col, cetearyl alcohol, phenoxyethanol, behentrimonium methosulfate, quaternium-91, and stearamidopropyl dimethylamine.

23. The method of claim **12**, wherein the maleic acid is present in an amount from about 1 wt % to about 10 wt % of the second active agent formulation.

24. The method of claim **1**, wherein following step (c) breakage of the hair is decreased by at least 5% compared to hair bleached with the bleaching formulation in the absence of the active agent.

25. The method of claim **1**, wherein following step (c) breakage of the hair is decreased by at least 10% compared to hair bleached with the bleaching formulation in the absence of the active agent.

26. The method of claim **1**, wherein following step (c) breakage of the hair is decreased by at least 20% compared to hair bleached with the bleaching formulation in the absence of the active agent.

27. The method of claim **1**, wherein following step (c) breakage of the hair is decreased by at least 40% compared to hair bleached with the bleaching formulation in the absence of the active agent.

28. The method of claim **1**, wherein following step (c) breakage of the hair is decreased by at least 50% compared to hair bleached with the bleaching formulation in the absence of the active agent.

29. The method of claim **1**, wherein following step (c), the hair is lighter compared to the hair prior to step (c).

30. The method of claim **1**, wherein the mixture does not comprise a dye precursor.

* * * * *

EXHIBIT C

L'ORÉAL USA, INC.

CONFIDENTIALITY AGREEMENT

May 15, 2015

Olaplex LLC
1482 East Valley Road
Suite 1701
Santa Barbara, CA 93108

Attn: Mr. Dean V. Christal

Ladies and Gentlemen:

We are interested in receiving certain non-public, confidential or proprietary information regarding LiQWD, Inc. (the "**Company**" or "**you**") in connection with a possible acquisition transaction of Olaplex LLC and/or the Company involving all or part of their respective equity or assets (the "**Transaction**"). Any such information disclosed, whether in writing or orally or by any visual, magnetic, electronic (including by way of an on-line data room) or other medium, by or on behalf of the Company or any of its Representatives (as defined below) to us or any of our directors, officers, employees, affiliates, debt financing sources and advisors of such party and those of its subsidiaries, affiliates and/or divisions (including, without limitation, attorneys, accountants, consultants, bankers and financial advisors) (collectively, "**Representatives**") in connection with such a Transaction is hereinafter referred to as the "**Confidential Information**".

The term "Confidential Information" shall be deemed to include without limitation (i) such information relating to technical data, research, product plans, products, services, suppliers, customers, know-how, developments, inventions, processes, designs, drawings, engineering, marketing, finances, notes, analyses or studies and all tangible and intangible embodiments thereof of any kind whatsoever, whether conveyed before or after the date of this letter agreement (the "**Agreement**"); and (ii) all reports, analyses, notes, compilations, forecasts, studies or other documents prepared by us or our Representatives to the extent that they contain or otherwise reflect such information ("**Notes**"). The term "Confidential Information" shall not, however, include information which (i) is or becomes generally available to the public other than as a result of disclosure by us or any of our Representatives in breach of the terms of this Agreement, (ii) was in the possession of us or any of our Representatives prior to the time it was first furnished to us or any of our Representatives by or on behalf of the Company or any of the Company's Representatives, (iii) becomes available to us or any of our Representatives from a source other than the Company or one of the Company's Representatives, provided we or such Representative does not know after reasonable inquiry that such source is bound by a confidentiality agreement with or has an obligation of confidentiality, whether legal or fiduciary,

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to the Company prohibiting such disclosure to us or such Representative with respect to such information or (iv) is or becomes independently developed by us or any of our Representatives without use of or reference to any Confidential Information. For purposes of clause (iv), the Company acknowledges that we (and/or our affiliates) may already possess or be developing products and/or services similar to, or competitive with, those of the Company.

NOW, THEREFORE, in consideration of the premises and the mutual agreements contained herein, the parties agree as follows:

1. **Restrictions on Disclosure and Use**. We will not disclose or permit our Representatives to disclose the Confidential Information to any person and will not use the Confidential Information for any purposes other than to evaluate, negotiate and, if applicable, consummate a possible Transaction, provided, however, that we may disclose Confidential Information to our Representatives who need to know the Confidential Information to assist us with such purposes and who are informed by us of the confidential nature of the Confidential Information and the confidentiality and non-use restrictions of this Agreement. We shall be responsible for any breach of this Agreement by our Representatives to the same extent as if they were parties hereto and shall take all reasonable measures (at our expense) to restrain our Representatives from making any unauthorized use or disclosure of any Confidential Information.

2. **Discussion Information**. Each party agrees that, without the prior written consent of the other party, it will not disclose to any person (other than its Representatives) the fact that the Confidential Information has been made available to us, that discussions or negotiations are taking place or have taken place concerning a possible Transaction involving us and the Company or any of the terms, conditions or other facts with respect to any such possible Transaction, including the status thereof and the identities of the parties thereto (collectively, the "**Discussion Information**"). You shall be responsible for any breach of this paragraph by your Representatives to the same extent as if they were parties hereto.

3. **No Representations or Warranties**. We acknowledge that none of the Company or its Representatives makes any express or implied representation of warranty as to the accuracy or completeness of the Confidential Information and the Company expressly disclaims any and all liability that may be based on the Confidential Information, errors therein or omissions therefrom. We agree that we are not entitled to rely on the accuracy or completeness of the Confidential Information and we agree that we shall be entitled to rely solely on the representations and warranties made to us in any definitive written agreement for the Transaction (the "**Transaction Agreement**").

4. **Return of Confidential Information**. Promptly upon the Company's request, all copies of the Confidential Information will be returned to the Company or, at our option, destroyed and all Notes will be destroyed, provided that neither we nor our Representatives shall be required to return or destroy any electronic copy of Confidential Information created pursuant to our or our Representatives' standard electronic or archival procedures in the ordinary course of business. Notwithstanding the foregoing, we and our Representatives may each retain copies of Confidential Information to the extent required to comply with legal or regulatory requirements (and, in the case of our accounting firms, any applicable professional standards) and each may retain copies of such information in the offices of its Legal Department to defend

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or maintain any litigation relating to this Agreement or the Confidential Information. Upon request, we will provide written notification to you of such destruction. Notwithstanding the return or destruction of Confidential Information pursuant to this Section 4, we will continue to be bound by the confidentiality and other obligations under this Agreement.

5. **Required Disclosure**. In the event that either party or any of such party's Representatives is requested or required (by law, stock exchange requirement, deposition, interrogatories, requests for information or documents in legal proceedings, subpoenas, civil investigative demand or similar process) to disclose any of the Discussion Information or Confidential Information, such party shall, to the extent permitted by law, provide the other party with prompt written notice (and, to the extent practicable, prior notice) of any such request or requirement so that it may seek a protective order or other appropriate remedy. Such party shall furnish only that portion of the Disclosure Information or Confidential Information which it is advised by counsel is so requested or required and will exercise its reasonable efforts to obtain reliable assurance that confidential treatment will be accorded to such Disclosure Information or Confidential Information.

6. **No License Granted**. Nothing in this Agreement is intended to grant any rights to us under any patent, copyright, trade secret or other intellectual property right nor shall this Agreement grant us any right in or to the Confidential Information, except the limited right to review such Confidential Information solely for the purposes of evaluating, negotiating and, if applicable, consummating a possible Transaction.

7. **Transaction Subject to Definitive Agreement**. The parties agree that unless and until a written definitive Transaction Agreement with respect to the Transaction has been executed and delivered, no party nor any of their Representatives shall have any legal obligation whatsoever with respect to any such Transaction (or any other transaction) by virtue of this Agreement or any other written or oral expression with respect to such Transaction by any of their directors, officers, employees or any other Representative except, in the case of this Agreement, for the matters specifically agreed to herein. Each party reserves the right, in its sole discretion, to reject any and all proposals made by the other party or any of its Representatives with respect to a possible Transaction, and to terminate discussions and negotiations with the other party or its Representatives at any time and for any reason or no reason. For purposes of this paragraph, the term "Transaction Agreement" does not include an executed letter of intent, memorandum or any other preliminary written agreement; nor does it include any written or oral acceptance of any offer or bid.

8. **Nonsolicitation of Employees**. Each of the parties covenants and agrees that during the eighteen (18) month period commencing as of the date of this Agreement, it will not, directly or indirectly, (a) employ, or seek to employ any of the other party's or its subsidiaries' employees with a title of Director or above (and, additionally in the case of the Company, Drs. Hawker and Pressly) , (b) encourage any of such employees (and, additionally in the case of the Company, Drs. Hawker and Pressly) to terminate their employment with the other party or its subsidiaries (and, in the case of Drs. Hawker and Pressly, their relationship with the Company and its subsidiaries); provided, however, that this Section 8 will not prevent a party from employing or retaining such persons who: (i) respond to general advertisements in newspapers and/or other media of general circulation (including, without limitation, advertisements posted

on the Internet) that is not targeted specifically at the employees, of the other party or its subsidiaries; or (ii) are referred to such party from recruiting firms or similar organizations engaged to identify and solicit persons for employment on its behalf of, so long as such recruiting firm or organization is not instructed to target any employees of the other party or its subsidiaries (and, additionally in the case of the Company, Drs. Hawker and Pressly).

9. **Entire Agreement; Amendments; Waiver**. This Agreement constitutes the entire agreement among the parties hereto relating to the subject matter contained herein, and supersedes all prior writings, discussions and understandings relating thereto. All modifications of, waivers of and amendments to this Agreement or any part hereof must be signed in writing by the Company and us. It is further understood and agreed that no failure or delay by any party in exercising any right, power or privilege hereunder, shall operate as a waiver hereof, nor shall any single or partial exercise thereof preclude any other or further exercise thereof or the exercise of any right, power or privilege hereunder.

10. **Severability**. In the event any provision or portion of this Agreement is determined to be invalid or unenforceable for any reason, in whole or part, the remaining provisions of this Agreement shall be unaffected thereby and shall remain in full force and effect to the fullest extent of applicable law.

11. **Term**. This Agreement, and all obligations hereunder, shall terminate on the earlier of (i) three (3) years from the date hereof and (ii) the entering into a Transaction Agreement between the parties hereto with respect to a Transaction; provided that any termination of this Agreement shall not relieve any breaches or other liability hereunder occurring during the term hereof.

12. **Governing Law; Jurisdiction**. This Agreement shall be governed by and construed in accordance with the laws of the State of Delaware without giving effect to its conflict of laws principles or rules. The parties hereby irrevocably consent to the exclusive jurisdiction of any state or federal court located within the State of Delaware over any dispute arising out of or relating to this Agreement and the transactions contemplated hereby and each party irrevocably agrees that all claims in respect of such dispute or any suit, action or proceeding relating thereto may be heard and determined in such courts. The parties hereby irrevocably waive, to the fullest extent permitted by law, any objection which they may now or hereafter have to the laying of venue of any such dispute brought in such court or any defense of inconvenient forum for the maintenance of such dispute. Each of the parties agrees that a judgment in any such dispute may be enforced in any other jurisdiction by suit on the judgment or in any other manner provided by law.

13. **Data Room and Other Confidentiality Requirements**. The terms of this Agreement shall control over any additional purported confidentiality requirements imposed by an offering memorandum or electronic database, data room, or similar repository of Information to which we or our Representatives are granted access in connection with this Agreement or a possible Transaction, notwithstanding acceptance of such an offering memorandum or submission of an electronic signature, "clicking" on an "I Agree" icon or other indication of assent to such additional confidentiality conditions, it being understood and agreed that we and our Representatives' confidentiality obligations with respect to the Information are exclusively

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governed by this Agreement and may not be enlarged except by an agreement executed by the parties hereto in traditional written format.

14. **Privileges**. To the extent that any Confidential Information includes materials or other information subject to the attorney-client privilege, work product doctrine or any other applicable privilege or doctrine concerning any pending or threatened action, suit, proceeding or government investigation or inquiry, you acknowledge that we have a commonality of interest with respect to such action, suit, proceeding, investigation, inquiry, arbitration or dispute, and agree that it is our mutual desire, intention and understanding that the sharing of such materials and other information is not intended to, and shall not, affect the confidentiality of any of such materials or other information or waive or diminish the continued protection of any of such materials or other information under the attorney-client privilege, work product doctrine or other applicable privilege or doctrine. Accordingly, all Confidential Information that is entitled to protection under the attorney-client privilege, work product doctrine or other applicable privilege or doctrine shall remain entitled to protection thereunder and shall be entitled to protection under the joint defense doctrine.

15. **Specific Performance; Attorneys' Fees**. It is further understood and agreed that money damages would not be a sufficient remedy for any breach of this Agreement and the non-breaching party shall, in connection with any determination that a breach has occurred, be entitled to equity relief, including, without limitation, injunction or specific performance as a remedy for such breach (without the need to post a bond or other surety in connection with such remedy). Such remedies shall not be deemed to be the exclusive remedies for a breach of this Agreement but shall be in addition to all other remedies available at law or equity to the non-breaching party. If a court of competent jurisdiction determines in a final, non-appealable order that this Agreement has been breached by a party or its Representatives, then such party will reimburse the other party for its reasonable, documented costs and expenses, including reasonable attorneys' fees.

16. **Assignment; Successors and Assigns**. Neither party may assign any of its rights or obligations under this Agreement to any person without the written consent of the other party hereto, except that the Company may assign this Agreement to any person who enters into a Transaction without our prior written consent. This Agreement will be binding upon and will inure to the benefit of the parties and their respective successors and permitted assigns.

17. **Joint Drafting**. This Agreement shall be construed as if jointly drafted and without regard to any presumption or rule requiring construction against the party who drafted it.

18. **Counterparts**. This Agreement may be executed in counterparts, each of which will be deemed to be an original copy of this Agreement, and all of which, when taken together, will be deemed to constitute one and the same agreement. Delivery of an executed counterpart signature page of this Agreement by facsimile or by PDF (portable document format file) shall be as effective as delivery of a manually executed counterpart of this Agreement.

[*Signature Page Follows*]

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If you are in agreement with the foregoing, please so indicate by signing and returning one copy of this Agreement.

Very truly yours,

Roger Dolden
SVP- Business Development

ACCEPTED AND AGREED
as of the date hereof:

LiQWD, Inc.

By: _____
Dean V. Christal
Title: President

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